Lateral Positioning and Wavelength Control of InP Based Quantum Wires and Dots

PROEFSCHRIFT

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To my dear wife, Yangfan
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Chapter 1

Introduction

1.1 Background

In the past decade, low-dimensional quantum structures have been extensively investigated. With the mature fabrication methods of molecular beam epitaxy (MBE), metalorganic vapor phase epitaxy (MOVPE), and chemical beam epitaxy (CBE), thin epitaxial films can be deposited with monolayer/sub-monolayer thickness control, accurate composition control, high material quality, and atomically abrupt interfaces. By this means, materials with excellent optical and electronic properties can be fabricated for applications in solid-state devices.

III/V compound semiconductors are of particular relevance due to their opto-electronic properties. GaAs and InP based materials cover the important 1.0–1.3 µm and 1.3–1.55 µm emission wavelength ranges, which are used for optical communication. To improve the opto-electronic properties of these materials, various new nanostructures such as quantum wells, wires, and dots (QWells, QWires, and QDs) were developed and investigated to exploit quantum effects. Compared to bulk materials, a quantum well structure is formed when a thin film with lower band gap energy is embedded in a barrier material with larger band gap energy. The thickness of the film is smaller than the de Broglie wavelength of electrons in the bulk material. Depending on the materials composition, the de Broglie wavelength is typically of the order of 10 nm, and the electron is confined in one dimension giving rise to new advantageous electronic properties. The energy dependence of the density of states changes from square-root to step-like dependence. Further reduction of the dimensionality makes these advantages more remarkable due to a more peak-shaped density of states.

The structures in which carriers are confined in two or three dimensions are called quantum wires (1D free motion) or quantum dots (0D free motion). The density of states of electrons for the bulk crystal ($\rho_{\text{bulk}}$), quantum well ($\rho_{\text{well}}$), quantum wire ($\rho_{\text{wire}}$), and
quantum dot ($\rho_{\text{dot}}$) structures, respectively, are expressed by

$$\rho_{\text{bulk}}(E) = \frac{(2m_e/h^2)^{3/2}}{(2\pi^2)^{1/2}} \sqrt{E},$$

$$\rho_{\text{well}}(E) = \sum_n \frac{m_e}{(\pi \hbar^2)} H(E - E_z(n)),$$

$$\rho_{\text{wire}}(E) = \sum_{n,l} \frac{(2m_e/h^2)^{1/2}}{\pi} \frac{1}{\pi} \left[ E - E_y(l) - E_z(n) \right]^{1/2},$$

$$\rho_{\text{dot}}(E) = \sum_{n,l,k} \delta(E - E_x(k) - E_y(l) - E_z(n)),$$

where $m_e$ is the effective mass of the electron, $E$ is the energy with respect to the bottom of the conduction band, and $E_z(n)$, $E_y(l)$, and $E_x(k)$ denote the quantized energy levels with quantum numbers $n$, $l$, and $k$, respectively; $\hbar$ is the reduced Planck’s constant; $\delta(E)$ is the delta function, and $H(E)$ is the Heaviside function, i.e. $H = 0$ for $E < 0$ and $H = 1$ for $E \geq 0$. The density of states of holes is “analogous”. Figure 1.1 shows the energy dependence of the density of states due to the different dimensionality of quantum confinement for bulk, quantum wells, wires, and dots.

Figure 1.1: Low-dimensional semiconductor structures and the corresponding energy dependence of the density of states.

Quantum wells have been studied extensively and are widely employed in devices such as edge emitting lasers, vertical cavity surface emitting lasers, quantum cascade
lasers, photodetectors, modulators and many more [1]. Quantum well lasers exhibit lower threshold currents compared to double heterostructures lasers due to the finite density of states above the optical band gap. The high structural and optical quality of quantum wells is ensured by the epitaxial growth technique providing excellent reproducibility. Extending the wavelength range on GaAs substrates into the important 1.55 µm telecom range, a 1.59 µm quantum well laser has been recently achieved using InGaNASb material as active region [2]. GaInNAs quantum well lasers can cover wavelengths ranging from 1.3 to 1.5 µm [3–5]. For these compounds, however, more studies are required to obtain optimized growth parameters. Hence, today’s telecom applications are dominated by the InP based materials system, the focus of this thesis, where wavelengths up to 1.65 µm are easily reached, as will be discussed in detail in the next chapter.

Compared to quantum wells, the additional lateral confinement in quantum wires results in heavy and light-hole intermixing and a saw-tooth shape of the density of states. The in-plane linear polarization in optical emission and absorption originating from the heavy and light-hole intermixing can be exploited for polarization sensitive devices. Further, enhanced state filling due to the peaked density of states and related enhanced optical non-linearity can be exploited for optical switching [6]. In the InP based materials system, self-organized lattice-mismatched InAs/InP quantum wires have been widely studied [7]. In this thesis, InGaAs sidewall quantum wires are fabricated on patterned InP (311)A substrates which exhibit distinct polarization behavior and enhanced nonlinear optical properties.

Quantum dots are the physical realization of a truly three-dimensionally quantum confined structure, which has atomic-like properties and therefore often is called an “artificial atom”. When the characteristic dimensions of such a system are less than the Broglie wavelength of the carriers, the energy levels become discrete, leading to a Kronecker delta-like density of states. The experimental realization of semiconductor quantum dots, made up of clusters of $10^3 - 10^4$ atoms for a typical diameter of around 20 nm, opens new research areas of bandgap engineering at the nanometer scale. Quantum dots can be fabricated by various techniques. Initially quantum dots were fabricated using electron beam lithography and dry etching whereby the quantum dot dimensions can be easily controlled, but the optical properties of these etched quantum dots are commonly poor [8–10] due to excessive nonradiative recombination of carriers at the rough and defected sidewalls. Moreover, defining the quantum dot pattern by, e.g., electron beam lithography and the processing are very time consuming, demanding other fabrication methods.

Today, quantum dots are mainly fabricated by strain induced self-organized growth of lattice mismatched material systems using MBE, MOVPE, and CBE. The lattice constant determines whether layers of different alloys can be grown epitaxially, which is the case for only a limited number of alloy combinations with the same lattice constant. However, a much wider range of materials becomes available if one allows strained thin layers. Since strain affects the band structure it can even be employed to enhance the optical properties of thin strained layers. The growth of thin layers of highly strained materials slightly above
the critical thickness results in strain relaxation through the formation of nanometer scale islands which often have the form of truncated pyramids or are lens shaped, depending on the growth conditions. Quantum dots are formed when these islands of smaller band gap energy material are embedded in a matrix of larger band gap energy. The optical properties of these quantum dots can be controlled by delicate structure design and tuning of the growth conditions. This enables the formation of a large variety of quantum dot structures. Typical quantum dot densities are in the range of $10^8 \text{ cm}^{-2}$ to $10^{11} \text{ cm}^{-2}$ with the quantum dots randomly distributed over the wafer surface. Upon the improvement of the growth technique, highly uniform quantum dots have been fabricated and, thus, applications based on quantum dots become more and more practical. A scheme of the growth mechanism, the Stranski-Krastanow growth mode, is presented in Fig. 1.2.

![Figure 1.2: Schematic diagram of the formation of quantum dots in the Stranski-Krastanow growth mode](image)

The three-dimensional quantum confinement and the resulting modification of the physical properties of quantum dots attracted many researchers to this interesting field. A lot of groups reported sharp optical emission lines from individual quantum dots due to the atomic-like confinement of excitons. Based on these physical properties, various device applications such as lasers, amplifiers, photodetectors have been attempted using quantum dots as active material. The optical properties of quantum dots are strongly influenced by the shape, size, density, and the spatial composition and strain distribution determined by the growth conditions such as substrate temperature, growth rate, annealing steps, growth interruptions, material composition, etc. Carrier re-distribution, state filling, and internal piezoelectric fields further determine the linear and non-linear optical properties of quantum dots, which will be addressed in this thesis.

InAs/GaAs quantum dot lasers were successfully achieved exhibiting low threshold current as theoretically predicted for systems with discrete energy levels [11]. High-speed optoelectronic devices have been realized and lasers with high temperature stability have been predicted and demonstrated [12]. Moreover, high carrier mobilities at room temperature in quantum dot superlattices with appropriate strength of electronic coupling have been predicted due to suppression of carrier scattering by optical phonons [13]. Figure 1.3 compares the advancements in the reduction of the threshold current density of bulk, quantum well, and quantum dot lasers [11]. Other areas of applications based on the properties of quantum dot ensembles include: mid-infrared detectors [14], semiconductor
optical amplifiers [15], and memory devices [16]. For InAs/GaAs quantum dots it turned out, however, to be difficult to reach the important 1.3–1.55 $\mu$m wavelength region for optical telecommunication systems without degradation of the optical properties. Therefore, in this thesis the In(Ga)As/InP materials system is exploited for the formation of quantum wires and quantum dots.

Figure 1.3: Decrease of the threshold current density of semiconductor injection lasers with different dimensionality of the active region over the years. [11]

In view of future quantum functional devices the lateral position control and ordering of quantum dots were improved by various delicate methods, especially by strain engineering and lithographic patterning. Ordered 1D quantum dot arrays [17–19] and 2D quantum dot molecules [20, 21] were successfully fabricated by self-organized anisotropic strain engineering of InGaAs/GaAs superlattice templates, which will be described in more detail in the next section and compared with other techniques based on lithographic patterning.

Quantum dots have been inserted into photonic cavities which can be based on photonic crystals (PhCs) [22–24], microcavity pillars [25, 26], and microdisks [27, 28] to fabricate novel structures exhibiting more interesting phenomena and properties. In these quantum dot microcavities, both the charge carriers and photons can eventually be confined in all the three dimensions. Structures that combine quantum dots and PhCs, enable the development of integrated optical systems [29] exploiting the optical properties of single quantum dot [23], and are promising candidates for the development of high-speed low-power-driven temperature-insensitive optical devices. They are also of interest for the modification of the quantum dot spontaneous emission rate through the Purcell effect [30].
and the study of quantum optics in solid state systems.

The optical properties of quantum dots inside high-quality (high-Q) factor microcavities are affected by the coupling of the photon electromagnetic field in the cavity with the quantum dot emitter. Enhanced quantum dot radiation into the resonant cavity mode will occur while radiation into other modes is suppressed. Microcavities with high-Q factors in the order of $10^4$ have been achieved. Therefore, the combination of quantum dots with microcavities might result in the development of novel optical devices to be used in all-optical networks.

Recently new types of nanostructures have been developed with the potential for different quantum effects resulting from new kinds of quantization of the electron and hole states. Nanorings were successfully fabricated by means of thin capping of quantum dots [31, 32] and droplet epitaxy [33–36]. The great interest in nanorings arises from the control of the interference of electron waves as a function of magnetic field which creates a vector potential changing the phase of the wave function, i.e. the well-known Aharonov-Bohm effect [37]. Recently this phenomenon was investigated for strained InAs/GaAs quantum rings formed by thin GaAs capping of InAs quantum dots [38]. Regarding droplet epitaxy, the group III element droplets are first formed on the substrate surface. Subsequently, the droplets react with the group V elements to generate the nanorings. This method has some advantages, such as growth at relatively low temperature and the fabrication of both lattice-matched and lattice-mismatched quantum dots and rings. Moreover, the liquid nature of the droplets tends to produce a larger variety of ring structure due to the diffusion and de-wetting mechanism, including concentric double rings, in contrast to the thin capping of quantum dots in lattice mismatched material systems.

Nanowires grown by catalyst-assisted chemical vapor deposition, strongly related to quantum wires, became another hot topic from the beginning of this century. With gold particles as catalyst, the deposited material grows locally in the so-called vapor liquid-solid mechanism to form nanowires with the catalyst on the top. Various characterization techniques, such as transmission electronic microscopy (TEM), cross-sectional scanning tunneling microscopy (X-STM), micro-photoluminescence (micro-PL) have been adopted to study the growth mechanism as well as the opto-electronic properties of the nanowires. A general review is provided in Ref. [39].

Clearly, low-dimensional nanostructures become more and more interesting and widely used for device applications. The work of this thesis focuses on advanced fabrication techniques and properties of quantum wires and quantum dots in the In(Ga)As/InP materials system like lateral position and wavelength control, which are essential for device applications in the important 1.55 $\mu m$ wavelength telecom region.
1.2 Patterned substrate

New approaches for lateral nanostructure formation combine different fabrication methods to overcome the existing technical obstacles and to obtain novel properties. By combining strain engineering with self-organized epitaxy techniques, laterally ordered 1D quantum dot arrays and 2D quantum dot clusters have been successfully achieved by Mano et al. and van Lippen et al. [17, 20]. However, it is still difficult to achieve precise position, density, and shape controlled quantum structures at wish. On the other hand, epitaxy on patterned substrates prepared by lithography and etching is one of the most powerful techniques to realize this. Growth on patterned substrates can overcome the disadvantages of randomly positioned self-organized structures. Therefore, a lot of studies were performed to fabricate low-dimensional quantum structures on pre-patterned substrates.

For pre-patterned substrates, if a selective growth mode exists in different areas, meaning that adatoms migrate preferentially between different areas on the surface due to different chemical bond strengths and migration lengths in areas with, e.g., different surface orientation, position controlled nanostructures are formed for optimized growth conditions. Moreover, due to the possible different degree of growth selectivity for different species of adatoms, well defined composition variations can take place. Several types of patterned substrates have been studied in-depth, including V-groove patterns, sharp ridges, T-shape patterns, and some more complex cases. Figure 1.4 schematically summarizes the growth processes on patterned substrates.

V-groove

V-grooves oriented along the [01-1] direction on (100) substrates are commonly patterned by photolithography and conventional wet chemical etching. The V-grooves are usually several μm wide and several 100 nm deep. For [01-1] oriented V-grooves, {111}A crystal planes are formed on the sides of the V-groove and the bottom of the V-groove approaches a (100) plane. During the growth, due to the smaller adatom migration length on the (100) plane compared to that on the {111}A sidewalls, the bottom of the V-groove becomes thicker leading to a crescent-shaped region, as has been modeled in detail [40]. In the case of GaAs/AlGaAs heterostructures, the carriers are laterally confined in the crescent-shaped GaAs region due to the lateral thickness variation of the of the GaAs quantum well which creates a lateral potential well. Therefore, the crescent-shaped quantum well acts as a quantum wire due to lateral quantum confinement for extensions of the crescent shaped region in the quantum size regime [41, 42]. For the vertical stacking of identical V-groove GaAs quantum wires, a relatively thick AlGaAs spacer layer has to be grown to re-sharpen the V-groove bottom. Inside the AlGaAs barrier layers, a vertical quantum well with reduced Al composition is observed, due to the faster Ga adatom migration towards the bottom of the V-groove compared to that of the Al adatoms. In photoluminescence (PL) and PL excitation (PLE) spectroscopy of V-groove quantum wires, a significant linear polarization anisotropy was observed confirming strong lateral carrier confinement [43]. V-groove quantum wire lasers have been fabricated [44] in the
Patterned substrate

GaAs/AlGaAs material system.

Ridge type

Ridge quantum wires are formed by selective epitaxy on mesa stripes prepared on (100) substrates by photolithography and wet or reactive ion etching. The depth and width of the etched mesa stripes are several µm, which is similar to the V-groove patterns, exposing {111} side facets. For the etched mesa stripe along the [011] direction, under certain growth conditions, (100)-{111}B facet structures appear. During growth, the (100) facet is diminished in width due to the migration of group III adatoms from the {111}B facets to the (100) plane resulting in a sharp ridge with {111}B side facets. After the sharp ridge structure is formed, an AlAs/GaAs/AlAs quantum well structure is deposited. The quantum well on top of the ridge is thicker than that on the {111}B side facets due to the migration of Ga adatoms from the {111}B facets to the (100) plane and the different angles of the incoming Ga flux. Therefore, electrons and holes are laterally confined in the thicker GaAs region on top of the ridge and, thus, this ridge structure acts as a quantum wire [45]. For mesa stripes oriented along the [01-1] direction, {111}A side-facets are formed and the quantum wire structure is realized similarly. However, experimental results indicate that the stripe orientation along the [011] direction is advantageous for the formation of quantum wire structures compared to that along the [01-1] direction because, for the [01-1] stripe orientation, macrosteps are easily formed on the {111}A side facets resulting in kinks in the quantum wires.

T-shaped

T-shaped edge quantum wires are formed by overgrowth of a cleaved edge plane. After the first epitaxy of a quantum well, the substrate is cleaved in the ultra high vacuum chamber to expose a (110) surface perpendicular to the (100) growth plane. The growth of a second quantum well is performed on this (110) surface. Therefore, the second quantum well together with the first one forms a “T” shape at the intersection where electrons and holes can be confined due to a local minimum of the quantization energy [46, 47]. However, due to the complicated growth procedure and the small area of the cleavage plane, further processing into device structures is difficult, especially when device integration is aimed for. Moreover, formation of a smooth cleavage plane can not be guaranteed, reducing the reproducibility for device applications. InAs quantum dots also have been grown on the cleavage plane, revealing some ordering which follows the multilayer structure of the first growth [48], but the luminescence efficiency of these quantum dots is low.

Sidewall

A complementary concept for realizing quantum wires and quantum dots is the selective growth on shallow-patterned high-index substrates. It was found experimentally that during growth of GaAs on mesa stripe patterned GaAs (311)A substrates processed by optical lithography and wet chemical etching, fast and slow growing sidewalls are formed depending on the orientation of the etched sidewall. For mesa stripes along the [01-1] direction, a fast growing sidewall appears on one side in the sector towards the next (100) plane,
while on the opposite side in the sector towards the next (111) plane, a slow growing side facet is observed. The fast growing sidewall exhibits a smooth and convex-curved surface profile without faceting. The fast growing sidewall forms due to preferential migration of Ga adatoms from the mesa top and bottom towards the sidewall. The slow growing sidewall, on the other hand, is formed due to preferential migration of adatoms away from the sidewall, resulting in a concave surface profile known from growth on patterned low-index substrates. Concave surface profiles are also formed on patterned vicinal (100) substrates [49], making it different from the formation of the fast growing sidewall on the patterned (311)A substrate. The unique growth mechanism of the fast growing sidewall can be used to fabricate quantum wires. When depositing a conventional GaAs/AlGaAs quantum well and choosing the height of the mesa stripe in the quantum size regime (several 10 nm), quantum wires are formed along the fast-growing sidewall of the mesas stripe oriented along the [01-1] direction [50].

Moreover, when atomic hydrogen is added during the formation of the fast growing sidewall, well ordered arrays of quantum dots are formed [51]. In atomic hydrogen assisted MBE growth of GaAs on GaAs (311)A substrates, a natural one dimensional surface corrugation on the nanometer scale is initiated. The direction of the surface corrugation is along [-233] which is perpendicular to the fast growing mesa sidewall on patterned substrates. The natural corrugation has a lateral periodicity of approximately 40 nm and is straight over several micrometers. Most important, the surface corrugation is also established on the convex-curved part of the fast growing sidewall. As a result, the quantum wires formed at the fast growing mesa sidewall in MBE are subdivided into pieces by the natural surface corrugation in atomic hydrogen assisted MBE to produce a one-dimensional array of dot-like nanostructures exhibiting a high degree of ordering as evidenced by photoluminescence measurements.

It should be noted that most of the quantum wire and quantum dot structures discussed above are fabricated on GaAs substrates with emission wavelengths shorter than 1.3 µm. To access the important 1.55 µm telecom wavelength region, quantum wire and quantum dot formation on shallow-patterned InP (311)A substrates is pursued in this thesis.

In general, growth on patterned substrates not only includes growth on substrates processed by lithography and etching (growth on non-planar substrates) but also growth on substrates patterned with dielectric masks (selective area growth). In selective area growth (SAG), after deposition of thin, typically 50–100 nm, dielectric masks such as SiO₂ or Si₃N₄ directly on the substrate surface, the mask is patterned using lithography and etching (wet chemical or Reactive Ion Etch). Selective area growth is then performed which, for optimized growth conditions, only occurs in the open areas. As for growth on non-planar substrates this allows for precise positioning and wavelength control of the nanostructures, relying on the growth rate enhancement in the open areas. Selective area growth is widely used for device applications, in particular for the direct monolithic integration of active and passive devices in a single growth step. Combined with local nanostructures formation, novel structures and, thus, new interesting functions for applications are expected. Strain
1.3 Scope of this thesis

The topic of this thesis is the lateral positioning and wavelength control of InP based quantum wires and quantum dots with emission wavelengths in the important 1.55 μm wavelength region, which rely on epitaxial growth techniques and strain engineered quantum wire and quantum dot formation in combination with patterning techniques including the fabrication of non-planar and masked substrates. Lateral position and wavelength control together with lateral ordering originate from selective growth mechanisms, i.e. local growth rate enhancements controlled by the substrate patterns. We demonstrate the formation of InGaAs quantum wires and InAs quantum dots on the fast growing sidewall of shallow-patterned high index InP (311)A substrates by CBE, and the locally controlled formation of InAs quantum dots on InP (100) substrate by selective area MOVPE (SA MOVPE). To examine the growth mode and structural material quality, various measurements were carried out, including atomic force microscopy (AFM), scanning electron microscopy (SEM), and cross-sectional scanning tunneling microscopy (X-STM). The optical properties were investigated in detail by temperature, excitation power, and polarization dependent macro- and micro-PL, exhibiting distinct features governed by the lateral carrier confinement in the quantum wires and quantum dots.

After providing a general background in Chapter 1, in Chapter 2 the basic materials properties of the InGaAsP/InP system are introduced. The different mis-oriented substrates used are compared, and important features of facets exposed in the growth on non-planar and masked substrates are described. The wafer preparation procedures are listed in detail and epitaxial growth by MBE, MOVPE, and CBE is compared. Moreover,
the characterization methods are briefly described, emphasizing the macro- and micro-PL setups.

In Chapter 3 we demonstrate the fabrication of (In,Ga)As sidewall QWires embedded in quaternary (Ga,In)(As,P) barriers, which is realized by CBE along [01-1] mesa stripes on shallow-patterned InP (311)A. The selective growth mode is examined and analyzed from the images and profiles taken by AFM and X-STM. The optical properties of the sidewall quantum wires are studied by micro- and macro-PL. The PL spectra reveal narrow line width, high efficiency, and large lateral carrier confinement energies of 60 – 70 meV. These large lateral carrier confinement energies are due to pronounced thickness and In composition changes relative to the adjacent quantum wells, as determined by X-STM in combination with micro-PL measurements. Moreover, the quantum wires are stacked in growth direction with identical PL peak emission energy. The PL emission energy is not only controlled by the (In,Ga)As layer thickness but also by the patterned mesa height. Stacked (In,Ga)As quantum wires with quaternary barriers exhibit room temperature PL emission at 1.55 µm in the technologically important wavelength region for telecommunication applications.

To further exploit and confirm the quality and optical properties of the sidewall quantum wires, detailed PL measurements were carried out of the stacked quantum wires, discussed in Chapter 4. Temperature dependent PL reveals efficient carrier transfer from the adjacent quantum wells into the quantum wires at low temperature, thermally activated repopulation of the quantum wells at higher temperature, and negligible localization of carriers along the quantum wires. Strong broadening of the power dependent PL spectra indicates enhanced state filling in the quantum wires compared to that in the quantum wells. Clear linear polarization of the PL from the quantum wires confirms the lateral quantum confinement of carriers.

In Chapter 5, formation and optical properties of highly strained InAs quantum dots embedded in InGaAsP formed at the fast-growing [01-1] mesa sidewall on InP (311)A substrates are investigated. Temperature dependent PL reveals efficient carrier transfer from the adjacent dash-like quantum dots in the planar areas to the larger sidewall quantum dots resulting in well-distinguishable emission around 80 K. The large high-energy shift of the PL from the sidewall quantum dots as a function of excitation power density is ascribed to the screening of the internal piezoelectric field. The linear polarization of the PL from the sidewall quantum dots is reversed compared to that of the quantum dashes in the planar areas due to the more symmetric shape and possible non-uniform strain in the sidewall quantum dots. Therefore, both quantum wires and quantum dots selectively formed on shallow-patterned InP (311)A substrates were successfully realized, exhibiting different morphologies and thus non-linear optical properties.

In addition to shallow substrate patterning, selective area epitaxy is exploited as an efficient method to realize lateral positioning and wavelength control of quantum dots. This is demonstrated in Chapter 6 for InAs quantum dots embedded in InGaAsP on InP (100) substrates by selective-area metalorganic vapor-phase epitaxy. The 1.55 µm wave-
length region is assessed by the combination of ultra-thin GaAs interlayers beneath the quantum dots with proper dielectric mask design. AFM and micro-PL reveal evolution of the quantum dots formed after small InAs supply as a function of growth rate enhancement in unmasked areas with pronounced height and density increase, resulting in a wide wavelength tuning range. Saturation of quantum dot formation is observed for larger InAs supply producing a much smaller wavelength tuning range which is supported by the increasing GaAs interlayer thickness. Hence, two regimes are identified allowing either wide wavelength tuning or wavelength stability in SA MOVPE of quantum dots in the 1.55 \textmu m region offering complementary applications.

Using a similar technique, in Chapter 7, we demonstrate the selective positioning of InAs quantum dots on InP pyramids grown by SA MOVPE. The positioning and number of quantum dots is controlled by inserting them at different growth stages in the InP pyramids. Micro-PL reveals distinct changes of the emission spectra as a function of the number of quantum dots. With reduced quantum dot number, the spectrum splits into ultra sharp peaks whose number correlates with the number of the quantum dots, revealing the emission of individual quantum dots in the of 1.5 \textmu m wavelength region at low temperature. Embedding the pyramids in lateral passive regrown InP/InGaAsP waveguide structures has been attempted, and the planarization behavior during regrowth after mask removal is discussed. This technique is promising for the fabrication of single photon sources operating in the 1.55 \textmu m region.

Finally, in Chapter 8 the thesis is summarized and concluded by a general comparison of the various methods for fabricating position and wavelength controlled quantum wires and dots in view of basic physics studies and device applications.

Bibliography


Chapter 2

Experiment

2.1 (Ga,In)(As,P) materials

One of the most important properties of many III-V compound semiconductor alloys is their direct bandgap ensuring efficient light generation. This enables optically active devices, in contrast to semiconductors with indirect bandgap such as silicon and germanium, dominating electronics. Well-known examples of the application of III-V semiconductors are light-emitting diodes (LEDs) and laser diodes (LDs) used, for instance, in displays, laser pointers, and ambient lightning. With the recent very rapid evolution of information technology towards the 21-century multimedia society, the demand for III-V materials and devices will obviously continue to expand. (Ga,In)(As,P) quaternary materials on InP provide the highest flexibility of independent lattice constant and wavelength control, however, the full understanding and exploitation of such complex systems is still developing. This is especially true for Al containing compounds which are important for high temperature operation of devices due to their better electron confinement.

For (Ga,In)(As,P) alloys on InP substrates, the most important advantage is the coverage of the technologically important 1.55 μm wavelength region [1]. This is the wavelength region of lowest absorption of silica-fibers on which today’s optical communication systems are based. Depending on the composition of the compound, the bandgap energy is in the range between 0.75 (In$_{0.53}$Ga$_{0.47}$As) and 1.35 eV at room temperature, which corresponds to wavelengths from 1.65 to 0.92 μm [2, 3], see Fig. 2.1. Thus, both transparent and absorbing or light-generating layers in the 1.55 μm region can be grown on the InP substrate. Additionally, by adding dopants, n- and p-type semiconducting or semi-insulating layers can be realized, and thus electrically driven devices can be fabricated. A certain quaternary compound, lattice matched to InP, is often identified by its emission wavelength, for example Q1.55 being the lattice matched (Ga,In)(As,P) alloy with a bandgap at $\lambda_Q = 1.55 \text{ μm}$.

When growth of thick layers is required, only lattice-matched alloys on InP are possible.
18  

$(Ga,In)(As,P)$ materials

Figure 2.1: Band gap energy versus lattice constant of various III-V semiconductors at room temperature (adopted from Tien 1988)

The lattice constant of InP at room temperature is 5.8694 Å, which is in between that of GaAs (5.6533 Å) and InAs (6.0583 Å). The InGaAs alloy lattice matched to InP has a fixed In composition of 53 %. Lattice matching for the quaternary alloy $Ga_xIn_{1-x}As_yP_{1-y}$ is satisfied for the condition $x(1.032-0.032y) = 0.47y$, which can be approximated by $y = 2.2x$ and allows the emission energies between 1.65 and 1.35 eV at room temperature. Detailed material parameters can be found in Ref. [4]. In this thesis, In(Ga)As compounds grown on lattice-matched InGaAsP/InP substrates are studied for formation of QWires and QDs emitting in the 1.55 µm telecom wavelength region.

InP based bulk and QWell structures are well-known and can be found in commercial products. QWire and QD structures are also extensively studied, mostly in the GaAs based materials system. However, due to the mature InP based processing techniques for photonic devices, QWires and QDs grown on InP are the most promising candidates for device applications in the telecom sector, not only for lasers but also for amplifiers, modulators, detectors, and so on. The conduction band offset at the InGaAsP/InP interface is about 40 % of the energy gap difference. This leads to a relatively small value of the conduction band discontinuity providing a low confinement energy for electrons within the quantum structure, resulting in electron overflow for high injection currents in laser operation and thermally activated carrier escape, which is the reason for the relatively low characteristic temperature $T_0$ of the threshold current [1]. On the other hand, InAs
QD structures on InGaAsP/InP may relieve parts of this disadvantage due to the peaked density of states, reducing carrier heating within the active region. The lattice mismatch between the compressively strained InAs and InP is 3.2 %, which leads to the 2D-to-3D growth mode transition when the InAs layer thickness is above the critical thickness of several monolayers and, thus, high quality QDs can be formed on the InP substrate. However, due to the smaller lattice mismatch compared to the InAs/GaAs system, the density of the InAs QDs formed on lattice-matched InGaAsP on InP of typically $3 \times 10^{10}$ is usually smaller than that on GaAs. The QD density can be improved by stacking QD layers in growth direction to increase the active volume which ensures sufficient gain of the QDs in active devices. Furthermore, by adopting the optimized lattice-matched InGaAsP alloy as waveguide core in active InGaAsP/InP double heterostructures, it is possible to fabricate new devices operating in the 1.55 µm range.

In contrast to the InGaAs/GaAs material system, the group V element (As/P) exchange during In(Ga)As growth on InGaAsP is an extra complicating factor, resulting in large chemical alloy composition variations, rough surface morphology, and very large InAs QDs especially at elevated substrate temperature. As a consequence, the optical quality of the QDs is usually poor and their emission wavelength is shifted to too large values beyond 1.65 µm at room temperature [5]. Therefore, a lot of work has been performed to form well-controlled InAs QDs on InP with the desired emission wavelength, such as by post growth annealing, double capping [6, 7], and the insertion of ultrathin GaAs interlayers to suppress As/P exchange [8]. In this way, self-organized InAs/InGaAsP/InP QD lasers in the 1.55 µm wavelength range were achieved by several groups in the last several years [9–11] with, however, so far still low characteristic temperature. This might be improved by further structural designs like the dot-in-well structure or the realization of tunnel injection. For further advanced device application, in particular the integration of active and passive devices based on InAs QDs, lateral positioning and wavelength control of QDs is required. In this thesis, this is achieved by employing CBE growth on patterned substrates and SA MOVPE.

### 2.2 Planes and facets

Substrates which are (100) oriented are widely used in research and for device applications. However, it is difficult to form laterally controlled QWires and QDs for this orientation due to the low surface anisotropy. Thus, scientists explored the growth on high index substrates which can exhibit a large surface anisotropy. High index substrates are cut along high Miller index planes. In contrast, substrates miscut by several degrees with respect to a low index plane are regarded as vicinal substrates. Figure 2.2 displays the atomic configuration of the (100) plane and some important high index planes viewed along the [0-11] direction. The angles between these planes are summarized in Table 2.1.

For the zinc-blende structures of III-V material systems, high index substrates of a
certain index may have two opposite orientations where the group element arrangement and the termination are reversed. Therefore, to distinguish between these surfaces, “A” or “B” are used to mark the group III terminated or group V terminated surface [3]. The different surface termination results in large differences in etching, mechanical, and crystal-growth properties. High index (N11) substrates have only one (0-11) cleavage plane, which is disadvantageous for device applications. The (311) substrate is one typical high index substrate with a high surface anisotropy. The mobility of adatoms during epitaxy along the two perpendicular directions, [01-1] and [-233], is different. After mesa patterning the substrate with stripes along the [01-1] direction, the two opposite sidewalls are not equivalent, which leads to a distinct selectivity of the epitaxial growth. Moreover, the atomic scale anisotropy also affects the growth selectivity and, in particular, the QD formation, leading to a complicated but interesting “dustpan” shape on the (311)A plane.

Figure 2.2: Planes with different orientations, viewed from the (0-11) cleavage plane

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>(111)</th>
<th>(211)</th>
<th>(311)</th>
<th>(411)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>54.7</td>
<td>35.3</td>
<td>25.2</td>
<td>19.5</td>
</tr>
<tr>
<td>(011)</td>
<td>35.3</td>
<td>54.7</td>
<td>64.8</td>
<td>70.5</td>
</tr>
</tbody>
</table>

Table 2.1: Relative angle between planes
The \{110\} and \{111\} are important planes for nanostructure formation. Figure 2.3(a) shows their arrangement relative to the (100) substrate surface. These facets are formed during InP pyramid growth in SA MOVPE discussed in Chapter 7. In cross-sectional SEM these facets are identified and distinguished by their angles with respect to the (011) or (0-11) cleavage planes and the (100) substrate surface, shown in Fig. 2.3(b). The angle relative to the (100) substrate surface is 35.3° for the \{110\} facet and 54.7° for the \{111\} facet.

![Diagram](image)

Figure 2.3: Definition of the crystallographic directions and planes relative to the (100) substrate (American Xtal Technology)

### 2.3 Epitaxy

#### 2.3.1 MBE versus MOVPE

For successful semiconductor device fabrication the epitaxial growth process must be controlled very accurately regarding both layer composition and thickness. For advanced nanostructures control even at the submonolayer level is required with high uniformity over the entire wafer surface, reproducible from run-to-run. Importantly, the electronic and optical epitaxial materials quality must be excellent to ensure good device performance.

In the last decade, both molecular beam epitaxy (MBE) and metal organic vapour phase epitaxy (MOVPE) have evolved to very important and mature techniques for fabricating III-V semiconductor heterostructures. MBE provides the most elementary process to grow crystals of high perfection. In MBE, the elemental or molecular sources are generated by thermal evaporation and the flux onto a heated substrate inside an ultra-high vacuum (UHV) growth chamber is controlled by the source temperature. At certain growth conditions, the resultant layer is epitaxial, which makes atomic scale control of surfaces and interfaces possible. The pressure in the growth chamber is below $10^{-5}$ Torr during
growth where the mean free path of the source materials is longer than the source to substrate distance (several tens of cm). Hence, the material transport is collision-free and occurs in form of atomic (Al, Ga, In) and molecular (As$_2$, As$_4$, P$_2$, P$_4$) beams. Abrupt shutter switching in front of the cells allows atomically abrupt interfaces. Therefore, fabrication of complex stacked structures becomes possible, especially quantum structures which require accurate control of the thickness of several to several tens of nanometers. Sources and substrates are degassed before growth to guarantee high materials purity. To maintain the UHV, various pumps are used, such as turbo pumps, cryo pumps, and ion pumps, together with the liquid nitrogen cooled shrouds. When opening the chamber to load new source materials, the chamber and sources are exposed to air. Therefore, baking and degassing are required to re-establish the UHV conditions, which is obviously time-consuming.

At typical growth temperatures between 400 and 650 °C for MBE, the sticking coefficient of the group III atoms in the case of GaAs and InP growth on the substrate surface is unity, while that of the group V materials, which are always provided in excess, is less than unity. Thus, the growth rate is determined by the arrival rate of the group III elements only. This makes it convenient to control the growth rate and composition of alloys. Reflection high energy electron diffraction (RHEED) is widely used in MBE to monitor the growth. With consumption of the source materials, the evaporation rate at a certain source temperature can change due to changes in the surface area and level. Thus, regular calibration of the growth rate is required, although optimized cell design reduces this problem. Moreover, changes in the growth rate within a certain layer stack requires temperature ramping during growth which might be critical due to unwanted annealing of the substrate.

In comparison, MOVPE, also called metal-organic chemical vapor deposition (MOCVD), uses vapor phase sources, which are transported by a carrier gas (commonly Hydrogen). Both MBE and MOVPE have their own characteristics, which originate from differences related to the type of sources and the working pressure. The gas flow in MOVPE is viscous and the chemicals reach the substrate by diffusion through a stagnant boundary layer. Reactor pressures range from 10 mbar (LP-MOVPE) to 1000 mbar (atmospheric pressure MOVPE), i.e. no UHV is required. To avoid gas turbulences, low-pressure horizontal or vertical reactor systems are used. A typical reactor for research work is composed of a radio-frequency (RF) or halogen lamp heated susceptor in a cold-wall quartz reactor. Trimethylgallium (TMGa), trimethylindium (TMIn) are generally used as group III precursors. For group V precursors, tertiarybutylarsine (TBAs) and tertiarybutylphosphine (TBP) are becoming popular as alternative sources to traditional group V hydrides (AsH$_3$ and PH$_3$) because they pyrolyse more rapidly at lower temperature, and are less toxic. Also the handling of these liquid source bubblers is much easier, and low V/III ratios and low-temperature growth can be achieved. Decomposition of the group III metal organic compounds (TMIn, TMGa) and the group V hydrides (TBAs, TBP) occurs by partial pyrolysis in the gas phase and further dissociation on the heated substrate surface.
usual growth temperatures (600 – 800 °C), the growth rate is limited by the diffusion rate of the group III alkyls through the boundary layer. Therefore, the reactor geometry must be carefully designed to provide a uniform flow pattern and perfect precursor mixing to ensure growth uniformity. The material flux into the reactor is regulated by electronic mass flow controllers or by pressure controllers, while valves are used for gas switching. Figure 2.4 depicts a schematic drawing of an MOVPE system. A detailed description of MOVPE is provided in Ref. [12].

Nowadays, MOVPE systems for high-throughput production are commercially available from a number of companies, especially in the semiconductor area. The use of vapor sources allows precise, stable, and reproducible control of flows. To overcome the memory effect of chemical sources, complicated gas switching systems have been designed. Another advantage of vapor sources is that they can be changed conveniently and without opening the growth chamber, in contrast to MBE. Moreover, the growth rate in MOVPE can be high, which is suitable for large scale and/or mass production, such as for LEDs and solar cells. In general, favorable economics require large-scale, high growth rates, and a high yield of suitable material (uniformity and reproducibility). Finally, MOVPE is the most versatile technique, suitable for the production of virtually all III-V semiconductor compounds and alloys. Nevertheless, several disadvantages remain in MOVPE, including the expensive reactants and the complex growth parameters which must be precisely tuned to guarantee the uniformity and reproducibility.

2.3.2 CBE

Various alternatives have been proposed in an attempt to combine the advantages of both MBE and MOVPE techniques. In contrast to standard MBE, the group V beams in gas source MBE (GS MBE) result from the thermal decomposition (cracking) of hydrides. Metal organic MBE (MO MBE), on the other hand, uses metal organic group III compounds which decompose on the heated substrate surface. Chemical beam epitaxy (CBE) combines a beam nature with the exclusive use of chemical precursors. This leads to a growth technique with unique and important properties, especially for selective area epitaxy (SAE). In these techniques, the sources are injected into a UHV system. Thus, the advantages and disadvantages of them are considered in the context of the effect of the reactor pressure on the MOVPE process.

Similarly to MBE, the large cryo shroud area provides excellent pumping efficiency for the source gases. This prevents contamination of the growing layer by species reflected or desorbed from the inner shell of the growth chamber. Since the pyrolysis happens when the source gases reach the substrate, it is an advantage over MOVPE, because memory effects are reduced when switching gases. Moreover, because of the high vacuum (< 10^{-4} torr), the beam-like characteristics of the injected gases are guaranteed. The pressure control and vent line (gas switching) design of the gas sources work much more accurately compared to the thermal control of evaporation precursors in MBE and, thus, regular
calibration of the flux rate is not required. Furthermore, the growth by MOVPE depends on the stagnant boundary condition, and thus edge defects are always observed, while this is reduced in CBE due to the beam nature as in MBE.

The group III alkyl molecules are introduced by a low temperature injector which is kept at 60 °C to prevent condensation. It produces a single beam that impinges directly onto the heated substrate surface (∼ 500 °C), where each molecule can either acquire enough thermal energy to dissociate all its three alkyl radicals, leaving the elemental group III atom attached on the surface, or desorb in undissociated or partially dissociated forms. The substrate temperature and the arrival rate of the metalorganics determine which process dominates: at sufficiently high temperatures, the growth rate is supply limited, while at lower substrate temperatures alkyl desorption determines the growth rate by site blocking. Due to the close cracking temperatures of AsH$_3$ and PH$_3$, the group V hydride flows are pre-mixed inside a high-temperature cracker (900 °C) before injecting to the growth chamber, where they are fully decomposed and form a single beam. A scheme of a CBE system is depicted in Fig. 2.5. Reference [13] systematically introduces CBE techniques.

The differences between MBE, MOVPE and CBE are reflected by significant differences in growth behavior. In MOVPE, the decomposition of the group III species starts in the gas phase, whereas the decomposition of the hydrides is mainly a surface reaction. On the other hand, the beam nature in CBE ensures that all reactions occur only in the high temperature cracker and on the hot substrate surface. In contrast to MOVPE, gas phase diffusion is excluded, and thus a very fast flow response can be achieved on the substrate surface. This makes it possible to grow atomically abrupt interfaces as in MBE and to study growth mechanisms using in-situ tools like mass spectrometry and RHEED. Another result from the absence of gas phase diffusion is that the selective area epitaxy in CBE is truly determined by the geometry of the open areas, while gas phase diffusion in MOVPE leads to a great growth enhancement due to sources being transferred from the masked to the open areas.

Compared to MOVPE, pre-cracking of the hydrides significantly improves the group V incorporation efficiency and the hydride consumption rate is strongly reduced. Also, the cracking efficiency of almost 100 % greatly reduces the amount of toxic gas to be treated in the exhaust. In addition, the substrate temperature can be kept much lower (500 °C instead of 650 °C). This is beneficial for the growth of structures with highly strained layers and prevents degradation of the initial structural quality and device performance in multiple step epitaxies. However, on the other hand, CBE also has its shortcomings. A consequence of CBE growth is that the growth parameter window is relatively narrow. The temperature range for the growth of lattice matched In$_{0.53}$Ga$_{0.47}$As on InP is about 30 °C, while the MOVPE window is 150–250 °C wide. Moreover, the layer compositions vary strongly with growth temperature. For the growth of lattice matched quaternary layers with a room temperature photoluminescence at 1.25 µm (Q1.25) this means that the temperature must be kept constant within a few °C. Therefore, an optical pyrometer
is generally used on CBE to monitor the substrate temperature.

Additionally, due to the above mentioned absence of gas phase diffusion and the relatively low growth temperature, the group V element (As/P) exchange in CBE is less strong than in MOVPE. Moreover, high reactor pressure and complex gas switching and gas exchange processes in MOVPE are not present in CBE, which also help to prevent the As/P exchange. In CBE, there is no complicated gas flow pattern across the substrate surface and the uniformity is directly related to the distribution of the beam profile and the temperature over the substrate area. In accordance with the premixing of the precursors, compositional uniformity is guaranteed. Therefore, low-dimensional quantum structures where the dimension and interface flatness at the atomic scale are important can be fabricated successfully as designed with excellent high optical efficiency. To summarize, the strengths and weaknesses of MOVPE and CBE are overviewed in Table 2.2.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Strengths</th>
<th>Weaknesses</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOVPE</td>
<td>Most flexible</td>
<td>Expensive reactants</td>
</tr>
<tr>
<td></td>
<td>Abrupt interfaces</td>
<td>Accurate parameter control needed</td>
</tr>
<tr>
<td></td>
<td>High purity</td>
<td>Hazardous precursors</td>
</tr>
<tr>
<td></td>
<td>Simple reactor</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Robust process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Uniform</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Large scale</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High growth rates</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Selective growth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In situ monitoring</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Widely used</td>
<td></td>
</tr>
<tr>
<td>CBE</td>
<td>Uniform</td>
<td>Low throughput</td>
</tr>
<tr>
<td></td>
<td>Abrupt interfaces</td>
<td>No large-scale reactors</td>
</tr>
<tr>
<td></td>
<td>Direct control of fluxes</td>
<td>Expensive reactants</td>
</tr>
<tr>
<td></td>
<td>In situ monitoring</td>
<td>Hazardous precursors</td>
</tr>
<tr>
<td></td>
<td>Selective growth</td>
<td>Hardly used</td>
</tr>
</tbody>
</table>

Table 2.2: Overview of MOVPE and CBE [12]

2.4 Selective area growth

More advanced methods can be used for growth on selective areas of the wafer. By placing a patterned silicon or metal “shadow mask” close to the substrate, the growth species can only reach the substrate surface through the mask openings [15]. A recent development in shadow masking is the use of epitaxial masks, consisting of a thick spacer layer and a masking layer on top. Selective underetching of the thick spacer layer provides
Selective area growth accurate mask windows. After regrowth, the mask and attachment on them are removed by a second selective etch. Disadvantages of the shadow mask approach are the sloped sidewalls surrounding the selectively grown structures and the alignment of the mask to previously grown structures. Further integration steps are also difficult because the surface after regrowth is non-planar.

A simple alternative approach is the selective area growth (SAG) using thin, typically 50–100 nm, dielectric masks such as SiO\(_2\) or SiN\(_x\), which are deposited directly on the substrate surface. Under certain growth conditions deposition is prevented on these dielectric masks. Patterning of the dielectric layer is done using standard photolithography and etching (wet chemical or Reactive Ion Etching (RIE)). Another technique is to grow a layer, etch away selected areas, and then regrow on this patterned surface. This is not only more complicated, but also frequently results in imperfect interfaces and damage in the regrown layer. The object of SAG is to have no deposition on the mask. However, growth of polycrystalline material on the mask can occur under certain conditions. For example, complete pyrolysis of the group III precursors results in the nucleation and thus deposition of either group III or III-V compounds on the mask. This is also why SAG is hardly achieved in MBE, but successfully used in MOVPE and CBE. Low reactor pressure decreases the extent of complete pyrolysis on the mask due to enhanced desorption, and thus LP MOVPE and CBE are suitable for SAG using flexible precursors and growth conditions. Increase of the mobility of group III molecules on the surface of the wafer can be accomplished by increasing the growth temperature, decreasing the V/III ratio, and lowering the partial pressure/growth rate which leads to faster desorption and/or less molecules on the surface.

In SA MOVPE, non-uniform depletion of the gas species in the boundary layer leads to concentration gradients in the region above the mask and that above the semiconductor. This affects the growth behavior by the filling factor, i.e. the ratio of the window to masked area, and by the widths of the windows and masks. The local growth rate is found to increase with decreasing window size and increasing mask area surrounding the window. Raised ear features are usually observed in the area close to the mask edges, extending over several micrometers into the open area, which is generally attributed to surface migration [16]. Therefore, both the gas phase diffusion and surface migration give a growth rate enhancement for the deposition in open areas. The enhanced growth mechanism is illustrated in Fig. 2.6.

Furthermore, besides the thickness enhancement, as the diffusion constants and migration lengths for the Ga and In species are different, the composition and homogeneity of locally deposited (qua)ternary material is affected. Thus, lateral bandgap engineering becomes possible. Figure 2.7 shows the connections between the geometric design and the band diagrams. Wavelength shifts are reported for bulk quaternary and quantum well structures [17–19]. SAG is an extremely powerful method for the growth of photonic devices and integrated circuits. Especially, for example, waveguide layers tailored for multiple wavelengths can be fabricated on the same chip without complex process-
ing. The active and passive region can be grown in one growth if local mask geometry is carefully designed. Useful applications are e.g. waveguide tapers for spot size converting to an optical fibre, integrated waveguide-modulator and waveguide-laser structures [20, 21]. Due to the potential of SAG, various studies using SEM, micro-PL, spatially resolved X-ray diffraction are performed in this research area, and advanced numerical simulations, involving a number of diffusion differential equations, allow to theoretically study the epitaxial behavior for given mask geometry.

Additionally, since mesa etching is not required for either laser device or waveguide fabrication, high uniformity can be obtained. Crystallographically perfect sidewalls and facets are obtained automatically. This is convenient for the growth of buried heterostructure lasers [22], and it also results in the formation of perfect facets for laser devices [23].

In comparison to SA MOVPE, SA CBE is truly area selectivity. The surface planarity and the uniformity of the composition homogeneity from the mask edge to the opening center are considerably higher [24], and independent from the mask geometry. For multiple step epitaxy, its lower growth temperature will decrease the deterioration of the underlying initial material quality, compared to SA MOVPE. Perfect selectivity is obtained under standard growth conditions.

2.5 Photolithography processing and sample preparation

The following steps are pursued to prepare the patterned substrate. This is also the standard process for InP passive waveguides. The substrate is cleaned in an oxygen plasma at 300 W for 10 minutes and etched in 1 H₃PO₄ : 10 H₂O for 2 minutes to remove the oxide layer. After rinsing the wafer in DI water and blowing dry in nitrogen, 100 nm silicon nitride is deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD). After depositing the SiNx layer, conventional photolithography is carried out to transfer the pattern from the photo-mask to the silicon nitride layer on the wafer.

After lithography, the silicon nitride layer is etched by RIE. To completely remove the photoresist, oxygen stripping for 30 minutes (at 300 W) is used. An additional dipping in 1% HF for 1 or 2 seconds removes any residues on the surface. After selective area growth, before the second growth (re-growth of the passive waveguide around the selectively grown active regions is discussed in Chapter 7) the SiNx is completely removed from the substrate in a 10% HF solution for 2 – 3 min. The sample is rinsed in DI water and blown dry. For patterning the non-planar InP (311)A substrate, we use wet chemical etching in 1 HCl : 10 H₃PO₄, with an etching rate of 50 nm/min. The surface profile is measured by an Alpha-stepper. The etching process can be repeated until the desired etch depth is reached. The whole process is summarized in the Table 2.3 and diagram of Fig. 2.8.
<table>
<thead>
<tr>
<th>Step</th>
<th>Equipment</th>
<th>Parameter</th>
<th>note</th>
</tr>
</thead>
<tbody>
<tr>
<td>stripper</td>
<td>TePla 100</td>
<td>300 W, 10 minutes</td>
<td>remove surface contamination</td>
</tr>
<tr>
<td></td>
<td>(oxygen plasma)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rinse</td>
<td>Etching bench</td>
<td>5 minutes in DI water</td>
<td>clean wafer</td>
</tr>
<tr>
<td>primer</td>
<td>HMDS setup</td>
<td>standard recipe 3 minutes and 15 seconds, 140 °C</td>
<td>get enough adhesion between the sample and the photoresist</td>
</tr>
<tr>
<td>spinning</td>
<td>Gyrset spinner</td>
<td>HPR 504, 3000 rpm, 50 acceleration, 30 seconds</td>
<td>spread positive photoresist</td>
</tr>
<tr>
<td>softbake</td>
<td>Hotplate</td>
<td>2 minutes and 30 seconds, 100 degrees</td>
<td>prepare photoresist for exposure</td>
</tr>
<tr>
<td>exposure</td>
<td>MA6</td>
<td>4.2 seconds at vacuum contact mode</td>
<td>exposure photoresist</td>
</tr>
<tr>
<td>postbake</td>
<td>Hotplate</td>
<td>115 °C, 2 minutes 30 seconds</td>
<td>prepare for development</td>
</tr>
<tr>
<td>develop</td>
<td>Etching bench</td>
<td>1 PLSI : 1 H2O, 75 seconds</td>
<td>transfer mask pattern to photoresist</td>
</tr>
<tr>
<td>rinse</td>
<td>Etching bench</td>
<td>5 minutes in DI water</td>
<td>remove residue from developed photoresist</td>
</tr>
<tr>
<td>descum</td>
<td>TePla 100</td>
<td>5 minutes, 50 W</td>
<td>sweep the corner of photoresist pattern</td>
</tr>
<tr>
<td></td>
<td>(oxygen plasma)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>hardbake</td>
<td>Hotplate</td>
<td>120 °C, 2 minutes</td>
<td>confirm the pattern being transferred to photoresist</td>
</tr>
</tbody>
</table>

Table 2.3: Photolithography processing procedure for mask production and detailed parameters

### 2.6 Characterization

Various spectroscopic equipment is employed for characterizing the size, shape, and optical quality of the QWires and QDs. Photoluminescence (PL), photoluminescence excitation (PLE), and X-ray diffraction measurements are routinely performed to determine the composition, dimension, and strain distribution of the semiconductor nanostructures. Atomic Force Microscopy (AFM) and Scanning Electron Microscope (SEM) provide the density, the spatial distribution, and the dimensions of the QWires and QDs. Spatially resolved information of the optical properties is obtained by micro-PL. The micro-PL setup consists of an imaging system, an x-y-z moving stage, and a single monochromator with an InGaAs charge coupled device detector (CCD). The sample is placed in a He-flow cryostat held at temperatures between 5 K and RT. The PL is excited by the 632.8 nm line of...
a He-Ne laser with excitation power of 10 µW through an optical microscope objective, which also serves to collect the PL. The excitation power can be controlled by internal neutral density filters. The spatial resolution is about 5 µm. The detection limit of the cooled InGaAs detector is 1.6 µm at -50 °C and 1.55 µm at -100 °C. The micro-PL system with xyz-stage is depicted in Fig. 2.9. Other specific characterization devices will be described in the chapters when they are employed.
Figure 2.4: Schematic drawing of a MOVPE system
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Figure 2.5: Gas handling system and growth chamber with in situ surface diagnostic capabilities incorporated in a CBE system [14]

Figure 2.6: Gas phase diffusion and surface migration for growth rate enhancement mechanisms in SA MOVPE
Figure 2.7: Illustration of monolithic integration of active and passive devices, $W_{ma}$ and $W_{mp}$ are the mask widths, $L_a$ and $L_p$ are the layer thicknesses, in the active and passive region respectively.
Figure 2.8: Diagram of pattern transfer by photolithography and etching
Figure 2.9: Schematic picture of the micro-PL system
Bibliography


Chapter 3

Sidewall Quantum Wires

3.1 Introduction

Quantum wires (QWires) are expected to have more interesting features compared to quantum wells (QWells) due to the superimposed lateral quantum confinement and, thus, peak-shaped density of states (DOS). QWires and quantum dots (QDots) with precisely controlled position and emission energy are strongly required for opto-electronic devices, such as lasers, modulators, detectors, etc., which is still a critical issue. A large variety of methods has been pursued in the last decade to achieve this goal. Self-organized strain-induced QWires are easy to form, but the density, position, and uniformity are difficult to control and to improve. Using lithographic techniques, position controlled nanostructures are easily fabricated, exploring, e.g., selective growth on patterned substrates. Most popular are the growth on V-groove patterned substrates [1–3] and the growth over sharp ridges [4–6]. A variety of theoretical and experimental work has been performed to improve the quality of V-groove and ridge-type QWires and QDots [7]. Both techniques rely on sharp corners or tips and, hence, relatively deep (typically several hundreds of nanometers) patterns, which are rounded in the case of V-grooves and sharpened in the case of ridges due to adatom migration from the adjacent slow-growing side facets towards the corners or tips for QWire and QDot formation. This requires re-shaping of the pattern during growth of the buffer and barrier layers with considerable thickness for well-defined QWire and QDot formation and stacking into multilayers [8, 9]. In addition, the sidewalls easily break up into micro-facets leading to undesired size fluctuations of the QWires and QDots. Most of the studies have been performed in the (Al,Ga)As/GaAs (100) material system. The growth of V-groove and ridge-type QWires and QDots in the technologically important (In,Ga)As/InP material system for opto-electronic devices clearly turned out

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to be even more difficult to control [10, 11]. A complementary concept for the formation of QWires and QDots has been previously developed on shallow-patterned GaAs (311)A substrates. Highly uniform quasi-planar GaAs/(Al,Ga)As QWires [12, 13] and QDots [14] have been realized by molecular beam epitaxy (MBE) at the fast-growing sidewall of [01-1] mesa stripes in the sector towards the next (100) plane with mesa heights of several tens of nanometers. QWire formation relies on the preferential adatom migration from the mesa top and bottom towards the sidewall, which is opposite in direction to that on V-groove or ridge-patterned (100)-oriented substrates [15]. The shallow etch depth minimizes processing induced damage for defect-free QWires and QDots. Due to the stable surface profile [16] minimal re-shaping is required for QWire and QDot formation and stacking, allowing barrier layers of any desired thickness. There might be a minimum barrier thickness to recover the surface profile which is, however, relieved compared to the case of V-grooves due to the quasi-planar nature of the sidewall quantum wire. Moreover, the absence of facet formation produces very smooth sidewalls and, thus, QWires and QDots with high uniformity and excellent optical properties up to room temperature.

Here we report the formation of highly uniform quasi-planar (In,Ga)As sidewall QWires by chemical beam epitaxy (CBE) on shallow [01-1] stripe-patterned InP (311)A substrates. The size and shape of the QWires are determined by cross-sectional scanning-tunneling microscopy (X-STM). The QWire thickness and In composition are enlarged at the mesa sidewall relative to those of the adjacent quantum well, which is analyzed by micro-photoluminescence (micro-PL) spectroscopy. Micro-PL reveals strong lateral carrier confinement in the QWires with InP and quaternary, lattice-matched (Ga,In)(As,P) ($\lambda_Q = 1.3 \mu m$) barriers. The lateral confinement energies are between 60 and 70 meV, deduced from the low-energy shift of the PL peak, which exhibits narrow linewidth and high efficiency. To increase the active volume, the QWires are stacked in growth direction with identical PL peak emission energy. The PL emission energy is controlled by the (In,Ga)As layer thickness and also the height of the patterned mesa stripes. Stacked QWires with quaternary barriers exhibit room temperature emission at 1.55 $\mu m$, demonstrating device quality of the (In,Ga)As sidewall QWires on shallow-patterned InP (311)A substrates with potential applications for fiber-based optical telecommunication systems.

3.2 Experiment

The (In,Ga)As sidewall QWires were fabricated by CBE on shallow-patterned InP (311)A substrates. [01-1]-oriented mesa stripes with 4 $\mu m$ width and 8 $\mu m$ pitch were prepared by photolithography and wet-chemical etching in the HCl:H$_3$PO$_4$ (1:10) solution. The mesa height was adjusted to 20–50 nm by the etching time with an etching rate of 50 nm/min. The patterned substrates were cleaned by oxygen plasma and then removing the oxide layer using H$_3$PO$_4$:H$_2$O (1:10) prior to overgrowth. For the CBE growth, trimethylindium (TMI), triethylgallium (TEG), AsH$_3$, and PH$_3$ were used as precursors. The AsH$_3$ and PH$_3$ gases were thermally decomposed in a high-temperature injector at 900 °C and the
TMI and TEG were introduced by a low temperature injector which is kept at 60 °C to prevent condensation. The InP substrates were mounted on Mo blocks by In condensation and degassed in the buffer chamber at 200 °C for 30 minutes before being transferred into the growth chamber. After oxide desorption, the substrate temperature was kept at 500 °C during the entire growth. The In$_{0.53}$Ga$_{0.47}$As and In$_{0.07}$Ga$_{0.27}$As$_{0.59}$P$_{0.41}$ ($\lambda_Q = 1.3 \mu m$, which is a common waveguide core material in InP-based photonic devices) layers for QWire formation with varied thicknesses and sequences, as specified below, were lattice-matched on planar InP. The structural properties of the QWires were determined by X-STM performed on the (01-1) cleavage plane in ultra-high vacuum in constant current mode. For the micro-PL measurements the samples were mounted in a He-flow cryostat. The PL was excited by the 632.8 nm line of a He-Ne laser with excitation power of 10 \(\mu\)W through an optical microscope objective, which also served to collect the PL. The spatial resolution was 5 \(\mu\)m. The PL was dispersed by a single monochromator and detected by a cooled InGaAs charge coupled device (CCD).

### 3.3 Selective growth mechanism

The growth mechanism was previously studied on GaAs substrate, shown in Fig. 3.1 [17]. Figure 3.2 depicts the AFM top view of the two opposite sidewalls of the mesa stripe along [01-1] after overgrowth. The fast growing sidewall where the QWires form is depicted in (a) and the slow growing one on the opposite side in (b). During (InP, (Ga,In)(As,P)) buffer layer growth, the fast growing sidewall evolves in the sector towards the next (100) plane. The surface exhibits a well-defined smooth convex-shaped profile, which provides the ideal template for (In,Ga)As QWire formation. This is due to the selective adatom migration towards this sidewall on the shallow-patterned (311)A substrates. On the opposite sidewall of the mesa, i.e. in the sector towards the next (111) plane, a slow growing sidewall develops and, thus, the surface breaks up into micro-facets with different orientations.

### 3.4 (In,Ga)As/InP QWires for formation analysis

#### 3.4.1 Structure

Figure 3.3 shows the X-STM image of a stack of three sidewall QWires formed by 10 nm thick (In,Ga)As layers at a 35 nm high mesa stripe. The InP buffer layer is 100 nm, the InP separation layers between the QWires are 50 nm, and the upper InP layer is 1 \(\mu\)m thick, n-type doped with Silicon for electron injection required for STM. The first 10 nm thick (In,Ga)As layer with 5 nm InP underneath marks the as-etched mesa profile in the sector towards the next (100) plane. The QWires exhibit a distinct thickness enhancement close to the sidewall to a maximum of 12–13 nm with an extension at the mesa bottom. This enhancement of the thickness is accompanied by In enrichment, as indicated by the
Figure 3.1: Growth mechanism on patterned GaAs (311)A substrates with mesa stripes oriented (a) along [01-1] and (b) along the perpendicular [-233] direction. The arrows indicate the preferential migration of Ga adatoms resulting in the formation of the fast-growing sidewall on the right-hand side of (a) and the formation of slow-growing side facets on the left-hand side of (a) and on both sides of (b) [17].

Height (brightness) contrast across the QWire width due to the corresponding compressive strain, leading to a proportional outward bending of the In containing structure at the cleavage plane [18]. The derived QWire thickness increase by a factor of 1.2–1.3 confirms the strong preferential migration of In and Ga adatoms from the planar areas towards the mesa sidewall, accompanied by In enrichment due to the larger In adatom migration length. An effective width of the tapered QWire of 200 nm is measured from the full-width at half-maximum of the thickness or In composition change across the QWire width in the
Figure 3.2: AFM images after overgrowth (a) of the fast growing sidewall where the QWire forms and (b) of the opposite slow growing sidewall

X-STM image. (In,Ga)As QWires are generally wider than GaAs ones [19], again due to the larger In adatom migration length.

Figure 3.3: X-STM image of the sidewall QWires formed by 10 nm (In,Ga)As embedded in InP on patterned InP (311)A substrate, viewed along [01-1].

3.4.2 Optical properties

The optical properties of the (In,Ga)As/InP sidewall QWires are examined for a 5 nm thick (In,Ga)As layer embedded in InP. The height of the mesa stripes is 35 nm, and the
thickness of the InP buffer and clad layer is 100 nm. The micro-PL spectra taken at 5 K from the planar area and the sidewall are shown in Fig. 3.4. The PL from the planar area exhibits a single peak centered at 0.918 eV, originating from the 5 nm thick lattice matched (In,Ga)As QWell. In contrast, the PL from the sidewall shows two well-separated peaks at the higher energy of 0.926 eV and at the lower energy of 0.862 eV from the QWell close to the sidewall and the QWire, respectively. The PL linewidth of the QWire of 19 meV is only slightly larger than that of the QWell of 15 meV. Together with the high PL efficiency and symmetric Gaussian line shape, this evidences the high uniformity and structural perfection of the QWire, with respect to thickness and composition. Certainly, in the GaAs based material systems narrower PL linewidths have been achieved indicating even higher uniformity. However, in the InP based system our sidewall quantum wires show PL lines having linewidths that are among the narrowest achieved. The slightly higher energy of the QWell PL close to the sidewall confirms the preferential migration of In and Ga adatoms from the planar areas towards the sidewall, causing adjacent QWell thinning and In composition decrease, as shown below.

Figure 3.4: Micro-PL spectra taken at 5 K from the planar area (upper curve) and from the sidewall (lower curve). The sidewall QWire is formed by 5 nm (In,Ga)As embedded in InP.
The large energy separation between the PL from the QWire and the adjacent QWell of 56 meV constitutes the lateral confinement energy of carriers in the QWire. It is comparable to that of GaAs QWires [12] although the thickness increase, i.e. confinement energy due to the vertical quantum-size effect of the tapered (In,Ga)As QWire is smaller. The thickness increases by a factor of two for the GaAs QWires and by a factor of 1.2–1.3 for the present (In,Ga)As QWire. This indicates, that a considerable contribution to the lateral carrier confinement energy stems from the increase of the In composition of the (In,Ga)As sidewall QWire, further reducing the optical transition energy. The opposite mesa sidewall reveals a negligible PL energy shift confirming the planarization due to preferential adatom migration away from this slow-growing shallow sidewall, which is similar to the behavior on (100)-oriented patterned substrates.

### 3.4.3 Thickness versus In composition increase

In order to unambiguously separate the contributions from the increase of the thickness and In composition to the lateral confinement energy, i.e. reduction of the optical transition energy of the QWire, a 50 nm thick (In,Ga)As layer is evaluated on the patterned substrate. The mesa height is 35 nm, and the InP buffer and cladding layers are 50 and 100 nm thick respectively. For such a (In,Ga)As layer thickness, the influence of thickness variations on the optical transition energy due to the vertical quantum size effect is not relevant and, thus, only changes in In composition play a role. Figure 3.5 shows the micro-PL spectra taken at 5 K from the (In,Ga)As layer in the planar area (upper curve) and at the mesa sidewall (lower curve). The small peak at higher energy in the spectrum from the sidewall is from the planar areas aside. The PL peak at the mesa sidewall, centered at 0.787 eV exhibits a low-energy shift of 20 meV compared to that in the planar area, which is centered at 0.807 eV, corresponding to lattice-matched In$_{0.53}$Ga$_{0.47}$As. This low-energy shift corresponds to a In composition at the mesa sidewall of 57 %, taking the biaxial compression of the strained (In,Ga)As layer into account.

The PL peak of the thick (In,Ga)As layer at the sidewall is as narrow as that in the planar area indicating a throughout homogeneous local In composition increase. Therefore, we take the same increase of the In composition for the compressively strained (In,Ga)As QWire to evaluate the lateral carrier confinement energy from the PL spectra in Fig. 3.4. Lateral quantum size effects are not taken into account due to the large width of the QWire resulting in a small contribution to the transition energy. Moreover, due to the large lateral width, the strain state of the QWire is assumed to be similar to that of strained QWells, i.e. it consists two parts: (i) biaxial strain along two perpendicular directions in the epilayer plane and (ii) uniaxial strain along the perpendicular (growth) direction. The in-plane strain is

$$
\varepsilon_{\parallel} = \frac{a_s - a_l}{a_l} = \varepsilon.
$$
Figure 3.5: Micro-PL spectra taken at 5 K from the planar area (upper curve) and from the sidewall (lower curve). The (In,Ga)As layer is 50 nm thick and embedded in InP.

The perpendicular strain is related to the in-plane strain $\varepsilon_\parallel$ through the Poisson ratio $\sigma$, as

$$\sigma = -\varepsilon_\parallel / \varepsilon_\perp.$$

Therefore, for cubic crystals grown on the (100) plane one gets

$$\sigma = \frac{c_{11}}{2c_{12}},$$

and

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_\parallel = \frac{a_s - a_l}{a_l},$$

$$\varepsilon_{zz} = -2\frac{c_{12}}{c_{11}}\varepsilon_\parallel.$$
\[ \varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{zx} = 0. \]

where \( c_{11} \) and \( c_{12} \) are the elastic stiffness constants, and \( a_l \) and \( a_s \) are the bulk lattice constants of the epilayer material and the substrate, respectively. For compressive strain \( \varepsilon \) is negative.

The energies of the conduction band and valence band edges as a function of hydrostatic strain are

\[ \Delta E_c = a_c (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = 2a_c \left(1 - \frac{c_{12}}{c_{11}}\right) \varepsilon \]

and

\[ \Delta E_v = -a_v (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = -2a_v \left(1 - \frac{c_{12}}{c_{11}}\right) \varepsilon \]

where \( a_c \) is the hydrostatic deformation potential in the conduction band and \( a_v \) that in the valence band. The energy shifts of the heavy hole and light hole bands due to the hydrostatic strain are the same. Further, due to the shear strain, the degeneracy of heavy hole and light hole bands will be lifted. The heavy hole band is shifted upward in energy, while the light hole band is shifted downward when the layer is compressively strained. The absolute energy shifts \( |Q| \) are the same with

\[ Q = -b \left(1 + 2 \frac{c_{12}}{c_{11}}\right) \varepsilon, \]

where \( b \) is the shear deformation potential. Taking into account these energy shifts induced by strain, the transition energy of the electron ground state to heavy hole ground state within the QWell or QWire, corresponding to the PL peak energy, can be calculated by solving the Schrödinger equation. For the QWell we assume lattice matched condition and thus only the width is varied for a constant composition of In\(_{0.53}\)Ga\(_{0.47}\)As, while for QWire we allow composition and thickness variation. The calculated emission energy as a function of layer thickness is plotted in Fig. 3.6. From the micro-PL measurement for the thick InGaAs layer, an In composition of 57 % at the sidewall is deduced. This allows only the width is varied. A QWire thickness increase to 6.5 nm is extracted from the difference of the QWire and QWell PL peak positions, taking into account the finite InP energy barrier height. This is 1.3 times the thickness of the 5 nm (In,Ga)As QWell, which is in agreement with the thickness increase of the QWire determined from X-STM. Hence, the lateral carrier confinement energy of the sidewall (In,Ga)As QWires on shallow-patterned InP (311)A substrates is governed by a 4 % enhancement of the In composition and a thickness increase by a factor of 1.2–1.3 due to preferential In and Ga migration from the mesa top and bottom towards the fast-growing sidewall, which is favored for In adatoms due to the larger surface migration length.
3.5 \((\text{In,Ga})\text{As}/(\text{Ga,In})(\text{As,P})\) QWires for photonic devices

3.5.1 Optical properties

The InP barrier layers of the sidewall QWires are replaced by lattice-matched quaternary \((\text{Ga,In})(\text{As,P})\) with \(\lambda_0 = 1.3\) \(\mu\)m, which is widely employed as waveguide core material in InP-based photonic devices. Figure 3.7 shows the micro-PL spectra taken at 5 K from the sidewall QWire formed by 3 nm \((\text{In,Ga})\text{As}\) with 120 nm lower and upper \((\text{Ga,In})(\text{As,P})\) barriers. The mesa height is 50 nm and the InP buffer layer thickness is 20 nm. The QWell layer thickness is reduced from 5 to 3 nm to shift the PL emission in the same energy region for the lower \((\text{Ga,In})(\text{As,P})\) energy barrier height. The upper PL spectrum with peak emission at 0.899 eV is taken from the planar area and the lower one from the sidewall with a peak centered at 0.903 eV from the adjacent QWell and a peak centered at 0.831 eV originating from the QWire. The slight high-energy shift of the QWell PL close to the sidewall and the large peak separation of the QWire and QWell emission reveal an unchanged formation mechanism of the \((\text{In,Ga})\text{As}\) sidewall QWire on \((\text{Ga,In})(\text{As,P})\) with an even larger lateral carrier confinement energy of 68 meV. This mainly results from the
thinner QWell layer, confirming that the QWire thickness enhancement and In enrichment are maintained. The linewidth of the sidewall QWire and QWell in the planar area are both reduced to 9 meV, again due to the reduced quaternary energy barrier height together with the high structural uniformity of the QWire. The lower energy barrier height leads to confined energy levels which are less sensitive to the interface fluctuation. In addition, some In enrichment in the quaternary (Ga,In)(As,P) layers above the sidewall, though not clearly observed in PL, cannot be excluded to further reduce the energy barrier height, contributing to the QWire PL low-energy shift and linewidth reduction.

Figure 3.7: Micro-PL spectra taken at 5 K from the planar area (upper curve) and from the sidewall (lower curve). The sidewall QWire is formed by 3 nm (In,Ga)As embedded in (Ga,In)(As,P).

3.5.2 Stacking

To increase the active volume, the QWires embedded in quaternary (Ga,In)(As,P) barriers are stacked in growth direction. The layer structure comprises a 20 nm InP plus 20 nm (Ga,In)(As,P) buffer followed by three 3 nm thick (In,Ga)As layers separated and overgrown by 50 nm (Ga,In)(As,P). The mesa height is 35 nm. The micro-PL spectra taken at 5 K from the planar area and the sidewall are shown in Fig. 3.8. The PL
spectra are very similar compared to those of the single sidewall QWire in Fig. 3.7. The linewidth of the PL spectrum of the QWires of 12 meV is only slightly larger and having a symmetric Gaussian line shape, indicating almost identical peak emission energy of all three stacked QWires. This is attributed to the stable surface profile, evolving during the thin buffer layer growth, which allows the vertical stacking of QWires with identical shape and In composition. This can also be observed from the X-STM image of Fig. 3.3. The fact that the stacked wires exhibit a slightly larger linewidth compared to the single ones might indicate some thickness and/or composition fluctuations. However, often also single quantum wires have linewidths of 12 meV, indicating that the structural changes are not systematic due to stacking.

Figure 3.8: Micro-PL spectra taken at 5 K from the planar area (upper curve) and from the sidewall (lower curve). The three-fold stacked sidewall QWires are formed by 3 nm (In,Ga)As embedded in (Ga,In)(As,P).
3.5.3 Emission energy control

In general, the emission energy can be tuned by designing the epitaxial layer thickness. Therefore, a wide range of wavelengths can be realized. Furthermore, tuning of the emission energy of the QWires is not only possible by the thickness of the (In,Ga)As layer but also by the height of the mesa stripes, which is adjusted by the etching process. Figure 3.9 depicts the peak emission energy at 5 K of the QWires as a function of the mesa height. The (In,Ga)As layer thickness is 3 nm, and the thickness of the lower and upper (Ga,In)(As,P) barriers on the 20 nm InP buffer is 120 nm. With increasing mesa height, the emission energy of the sidewall QWires continuously shifts to lower energies, starting to saturate above a mesa height of 50 nm. Hence, the thickness and In composition of the QWires are enhanced when the height of the mesa stripe is increased in the several tens of nanometers range. This is attributed to a steeper surface profile after buffer layer growth since the total sidewall height remains unchanged during overgrowth. For too high mesa height, the growth selectivity saturates and decreases when the accumulation of In and Ga adatoms at the sidewall becomes limited by the migration length. The dependence of the emission energy on the mesa height, furthermore, explains the small difference in PL peak position of the single and triple QWires in Fig. 3.7 and Fig. 3.8. The linwidth as a function of mesa height as shown in Fig. 3.9 does not show a systematic dependence, indicating no systematic changes of the structural quality of the quantum wires.

3.5.4 1.55 µm emission at room temperature

Figure 3.10 shows the PL spectra taken at room temperature of the same three-fold stacked sidewall QWire structure that gave the PL shown in Fig. 3.8. The upper PL spectrum of the QWells in the planar area exhibits a peak emission at 0.840 eV due to the electron-heavy hole transition and a shoulder at 0.890 eV originating from the quaternary (Ga,In)(As,P) barriers. The peak intensity drops by a factor of 1000 between 5 K and room temperature due to thermally activated carrier escape. At the sidewall, the PL spectrum reveals a clear shoulder at lower energy due to the emission from the QWires. Using a Gaussian fit, a peak energy of 0.80 eV is determined, corresponding to the emission wavelength of 1.55 µm. Hence, the large lateral carrier confinement energy, excellent uniformity, increase of the active volume by stacking, and emission energy control by the mesa height demonstrate device quality of the (In,Ga)As sidewall QWires in (Ga,In)(As,P) for photonic devices operating in the 1.55 µm wavelength region at room temperature.
Figure 3.9: Dependence of the emission energy and linewidth at 5 K of the sidewall QWires on the height of the patterned mesa stripes. The QWires are formed by 3 nm (In,Ga)As embedded in (Ga,In)(As,P).

### 3.6 Conclusion

We have fabricated quasi-planar (In,Ga)As sidewall quantum wires (QWires) along [01-1] mesa stripes on shallow-patterned InP (311)A substrates by chemical beam epitaxy (CBE). The structural analysis by cross-sectional scanning tunneling microscopy (X-STM) revealed thickness increase and In enhancement close to the mesa sidewall, which has been precisely evaluated by micro-photoluminescence (micro-PL) spectroscopy. The QWires embedded in InP and lattice-matched quaternary (Ga,In)(As,P) barrier layers revealed narrow PL linewidths, high PL efficiency, and large lateral carrier confinement energies. The QWires have been stacked in growth direction with identical PL peak energies. The emission energy of the QWires has been controlled by the (In,Ga)As layer thickness and the height of the patterned mesa stripes. Room temperature PL emission centered at 1.55 µm has been demonstrated for stacked QWires embedded in (Ga,In)(As,P) barriers. Hence, the potential of (In,Ga)As sidewall QWires on shallow-patterned InP (311)A substrates for photonic devices operating in the 1.55 µm telecommunication wavelength region is established.
Figure 3.10: Micro-PL spectra taken at room temperature from the planar area (upper curve) and from the sidewall (lower curve). The three-fold stacked sidewall QWires are formed by 3 nm (In,Ga)As embedded in (Ga,In)(As,P). The dashed lines in the lower spectrum are Gaussian fits.

Bibliography


Chapter 4

Optical Properties of Stacked Sidewall Quantum Wires

4.1 Introduction

In the previous chapter, we have described the fabrication of highly uniform InGaAs sidewall QWires in InGaAsP on shallow [01-1] mesa-patterned InP (311)A substrates. Preferential migration of In and Ga adatoms towards the mesa sidewall produces QWires with thickness enhancement by a factor of 1.2–1.3 and 4 % enrichment of the In composition compared to that of the adjacent lattice-matched InGaAs quantum wells (QWells) has been observed. The width of the tapered QWires is about 200 nm, which has been determined by cross-sectional scanning tunneling microscopy (X-STM) and photoluminescence (PL) measurements [1]. Here we present detailed temperature, power, and polarization dependent PL measurements of the three-fold stacked InGaAs sidewall QWires with room temperature (RT) PL peak wavelength at 1.55 \( \mu \text{m} \) required for applications in fiber-based optical telecommunication systems. Efficient carrier transfer from the QWells into the QWires at low temperature, thermally activated repopulation of the QWells at higher temperature, negligible carrier localization along the QWires, and enhanced state filling in the QWires is deduced from temperature and power dependent PL. Lateral quantum confinement of carriers in the QWires is confirmed by a clear linear polarization of the PL.

The QWire structure selected for the present study comprises a layer structure consisting of a 20 nm InP plus 20 nm lattice-matched In\(_{0.73}\)Ga\(_{0.27}\)As\(_{0.59}\)P\(_{0.41}\) buffer with bandgap at 1.3 \( \mu \text{m} \) (Q1.3) which is followed by three 3 nm thick lattice-matched In\(_{0.53}\)Ga\(_{0.47}\)As lay-

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ers separated and overgrown by 50 nm lattice-matched Q1.3 InGaAsP. For PL, the sample was placed in a He-flow cryostat and excited by the 532 nm line of a Nd:YAG laser at temperatures between 10 K and RT and excitation power density between 2.5 and 250 mW/cm$^2$. The PL was dispersed by a single monochromator and detected by a cooled InGaAs charge-coupled device (CCD). A linear polarizer followed by a quarter-wave plate was inserted in the detection path directly after the sample to analyze the linear polarization of the PL.

4.2 Temperature dependent PL

When carriers are excited in a semiconductor (optically or thermally), the minority carriers diffuse over a mean distance before recombination, which is called the diffusion length. Carrier transfer between the QWires and adjacent QWells is due to drift-diffusion processes, where both the carrier concentration gradient and the effective electric field resulting from the lateral carrier confinement act as driving forces. This is described by the following equation

$$\frac{dn}{dt} + D \frac{d^2n}{dx^2} = -\frac{n}{\tau} + c,$$  \hspace{1cm} (4.1)

where $n$ is the number of excitons, $D$ is diffusion coefficient, $\tau$ is the lifetime, and $c$ is the generation rate of excitons.

However, due to many unknown factors and boundary conditions a quantitative solution describing the experimental situation is difficult to obtain. However, it allows a qualitative understanding of the physical process occurring in the temperature dependent and power dependent PL measurements.

Figure 4.1 shows a series of PL spectra as a function of temperature. The excitation power density is 250 mW/cm$^2$. A schematic drawing of the QWire structure is depicted in the inset. The line at lower energy is from the QWires at the fast-growing mesa sidewall and that at higher energy from the adjacent QWells. The weak line in-between stems from the opposite slow-growing mesa sidewall which quickly smears out during growth [1]. At low temperature, the PL lines of the QWires and QWells are well separated, allowing to accurately determine the PL intensity and peak energy. At higher temperature the PL intensity and peak energy are determined by line fitting. With increase of the temperature from 10 to 60 K, the integrated PL intensity of the QWires increases while that of the QWells decreases, as plotted in Fig. 4.2 (a). The emission from the slow-growing sidewall vanishes. The total integrated PL intensity stays almost constant. This reveals efficient carrier transfer from the QWells and the slow-growing sidewall to the QWires upon temperature rise which is attributed to thermally activated delocalization of carriers in the QWells and at the slow-growing sidewall, and the intrinsic increase of the carrier diffusion length $L = \sqrt{D\tau}$ in the QWells in this temperature range [2].
Figure 4.1: PL spectra of the QWires and QWells as a function of temperature. The inset shows a schematic drawing of the QWire structure.

Above 80 K, the integrated PL intensity of the QWires decreases relative to that of the QWells which is depicted in Fig. 4.2 (b) by the ratio of QWell to QWire integrated PL intensity as a function of temperature, undergoing a minimum around 80 K. This reflects the decrease of the carrier diffusion length at higher temperature and, more important, thermally activated repopulation of the QWells, similar to the case of GaAs sidewall QWires [2]. The total PL intensity decreases above 60 K up to RT by about three orders of magnitude due to thermally activated transfer of carriers to the InGaAsP barriers, generally observed for QWells, QWires, and QDots. The ratio of QWell to QWire integrated PL intensity increases to about two at RT [1].

The temperature dependence of the energy shift of bulk semiconductors can be expressed by the expression (Varshni law),

$$E(T) = E(0) - \alpha T^2 / (T + \beta),$$

where $\alpha$ and $\beta$ are fitting parameters characteristic of a given material, and $E(0)$ is the band gap at zero temperature. Ideally, an equal energy shift is expected for quantum confined structures, in the absence of carrier localization. It should be noted that the Varshni law is an empirical expression to describe the energy shift. Especially, at low temperature, many experimental results reveal a rather constant energy in contrast to the Varshni law. Therefore, other expression to better describe the band gap shift have been proposed by O’Donnell [3]

$$E(T) = E(0) - S\langle \hbar \omega \rangle [\coth(\langle \hbar \omega \rangle / 2kT) - 1],$$
where $S$ is a dimensionless coupling constant and $\langle \hbar \omega \rangle$ is an average phonon energy.

The temperature dependence of the PL peak energy of the QWires shown in Fig. 4.3 almost perfectly follows the temperature dependence of the band gap energy described by the O’Donnell expression (solid line in Fig. 4.3). Only a very weak indication of an “S”-shape like dependence is observed. “S”-shape like temperature dependence originates from thermally activated carrier delocalization in the presence of potential fluctuations due to inhomogeneities in size and composition of QWells, QWires, or QDots [4]. The preferential population of lower-energy sites results in enhanced low-energy shift of the
PL peak at intermediate temperatures. Hence, the absence of such “S” - shape like temperature dependence of the PL peak energy demonstrates high uniformity of the present QWire structure along the mesa sidewall.

![Temperature dependence of the PL peak energy of the QWires.](image)

**Figure 4.3:** Temperature dependence of the PL peak energy of the QWires.

### 4.3 Power dependent PL

Figures 4.4 (a) and (b) show the power dependent PL spectra of the QWires and QWells taken at low temperature (10 K). With increase of the excitation power density from 2.5 to 250 $mW/cm^2$, the full-width at half-maximum (FWHM) of the QWires broadens by 8 meV while that of QWells remains unchanged, as plotted in Fig. 4.5 (a). Moreover, the PL peak energy of the QWires shifts to higher energy by 4 meV while it stays constant for the QWells in the excitation power density range under consideration (Fig. 4.5 (b)). In the present QWire structure, piezoelectric effects can be neglected to account for the PL high-energy shift due to the small lattice mismatch of less than 0.3 % [5, 6]. This is confirmed by the fact that the low-energy side of the PL spectra is unchanged, and the PL spectra broaden towards higher energy. Hence, we conclude that the observed broadening and high-energy shift of the PL from the QWires with excitation power density is due to enhanced state filling in the QWires compared to that in the QWells reflecting the transition from the two-dimensional step-like DOS of QWells to the one-dimensional peaked DOS of QWires. For a quantitative evaluation of the state filling the carrier density in the quantum wires is required. The carrier density, however, is governed by the complex carrier diffusion and capture effects which cannot be resolved by the present experiments demanding higher spatial resolution such as achievable by SNOM. Therefore the excitation power density is used as a phenomenological parameter to characterize the enhanced state filling of the quantum wires.
4.4 Linear polarization dependent PL

The in-plane linear polarization of the emission from QWires is an important property, reflecting the lateral carrier confinement, leading to heavy and light hole intermixing [7, 8]. In order to determine the degree of polarization, the optical transition matrix element provided by the electron and hole wavefunctions needs to be calculated. Neglecting the electron-hole interaction, i.e. excitonic effect and supposing the band gap energy and split-off energy are large enough to prevent the coupling between the conduction band
and the heavy- and light hole bands and the split-off band, we only consider the coupling between the heavy and light hole bands. For simplicity it is assumed that the confining potential can be written as \( V(x,z) = V_x(x) + V_z(z) \). \( x \) and \( y \) are the in-plane coordinates (\( y \) along the QWire direction) and \( z \) is the vertical coordinate (growth direction). In the conduction band, the electron wavefunction in the envelope function approximation and the corresponding energy states \( E = E_x + E_y + E_z \) are determined by the differential equations.
The valence band is described by the Luttinger and Kohn model,

$$H = \begin{bmatrix} H_h & c & b & 0 \\ c^+ & H_l & 0 & -b \\ b^+ & 0 & H_l & c \\ 0 & -b^+ & c^+ & H_h \end{bmatrix} \begin{bmatrix} \frac{3}{2} \\ \frac{1}{2} \\ \frac{1}{2} \\ \frac{3}{2} \end{bmatrix}$$ \tag{4.2}

where

$$H_h = \frac{\hbar^2}{2m_0}[(\gamma_1 + \gamma_2)(\partial_x^2 - k_y^2) + \partial_z(\gamma_1 - 2\gamma_2)\partial_z] + V_x(x) + V_z(z)$$ \tag{4.3}

$$H_l = \frac{\hbar^2}{2m_0}[(\gamma_1 - \gamma_2)(\partial_x^2 - k_y^2) + \partial_z(\gamma_1 + 2\gamma_2)\partial_z] + V_x(x) + V_z(z)$$ \tag{4.4}

$$b = \frac{\hbar^2\sqrt{3}}{2m_0}(\partial_x + k_y)(\gamma_3\partial_z + \partial_z\gamma_3)$$ \tag{4.5}

$$c = -\frac{\hbar^2\sqrt{3}}{2m_0} \frac{\gamma_2 + \gamma_3}{2}(\partial_x + k_y)^2$$ \tag{4.6}

$\gamma_1$, $\gamma_2$, and $\gamma_3$ are the Luttinger parameters.

The linear polarization dependent PL spectra of the QWires and QWells taken at low temperature and RT are depicted in Fig.s 4.6 (a) and (b). The excitation power density is 250 mW/cm$^2$. In the spectra taken at low temperature, the PL from the QWires (PL peak at 0.85 eV) is clearly polarized along the [01-1] direction, i.e. along the QWire axis, whereas the polarization of the PL from the QWells and from the smeared-out slow-growing mesa sidewall (small peak in-between) is negligible. The degree of linear polarization of the PL from the QWires, defined as

$$\rho = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp}$$ \tag{4.7}

is 0.09, where $I_\parallel$, and $I_\perp$ are the PL intensities for linear polarization parallel and perpendicular to the QWires.

At RT, the degree of linear polarization of the PL from the QWires is increased to 0.13 (PL peak at 0.80 eV in Fig. 4.6 (b)). This evidences that the polarization anisotropy of the PL from the QWires is of intrinsic nature and not, e.g., related to anisotropic localization sites effective at low temperature. For the QWells, the electron-heavy hole transition (PL peak at 0.85 eV in Fig. 4.6 (b)) reveals a weak degree of linear polarization of -0.03 along [2-3-3] while the electron-light hole transition (0.90 eV) is weakly polarized along [01-1], due to the valence band anisotropy in the (311) plane [9]. The PL of the bulk InGaAsP barriers (0.94 eV) is unpolarized. The linear polarization anisotropy of the PL from the QWires is in agreement with lateral quantum confinement effects, causing a mixing of
Figure 4.6: Linear polarization dependent PL spectra taken (a) at 10 K and (b) at room temperature (RT). The solid and dashed lines indicate the linear polarization along and perpendicular to the QWire axis.

the heavy-hole and light-hole energy states. Before a definite conclusion, however, other possible contributions have to be discussed.

The presence of biaxial compressive strain in the QWires, i.e. in-plane lattice compression such as in strained QWells in itself does not create polarization anisotropy. It rather decreases linear polarization effects by increasing the energy separation between heavy-hole and light-hole states. The piezoelectric field induced by the biaxial compressive strain
in the QWires has an in-plane component along the [2-3-3] direction, i.e. perpendicular to the QWire axis [6]. Hence, the effect of the piezoelectric field is to induce linear polarization perpendicular to the QWires which is perpendicular to the observed one. Moreover, due to the small lattice mismatch of less than 0.3 % pronounced piezoelectric effects are not expected nor observed in the power dependent PL measurements. Triaxial strain in the QWires, i.e. including (non-uniform) strain perpendicular to the QWire axis can cause linear polarization of the PL along the QWires. Notomi et al. analyzed the contribution of strain and lateral width to the degree of polarization for a highly strained InAsP/InP QWire. The study indicates that triaxial strain enhances the polarization along the QWire while biaxial strain suppresses it, and that the degree of polarization due to strain decreases strongly with increasing lateral width of the QWire [10]. However, again due to the small lattice mismatch, strain cannot account for the observed magnitude of the degree of linear polarization in our QWire structure [5].

H. Ikada et al. [11] fabricated diluted magnetic semiconductor ZnCdMnSe/ZnSe QWires by electron beam lithography and wet chemical etching, and they attributed the large polarization degree (40 % ∼ 90 %) to the dielectric grating effect. Due to the grating effect, the $E$ component of the incident light becomes anisotropically distributed after diffraction. However, electromagnetic (grating) effects can be excluded for our quasi-planar QWire structure and would affect the QWire and QWell PL similarly [12]. Therefore, we conclude that the linear polarization of the PL from our QWires indeed stems from lateral quantum confinement. It is interesting to note that the degree of linear polarization indicates an effective width of the lateral extension of the ground state wave-function in the QWires of less than 100 nm [10, 13]. This is considerably smaller than the geometrical width of the QWires of 200 nm deduced by X-STM. The effective QWire width is determined by the precise lateral In composition profile and thickness change, which are difficult to evaluate by X-STM, and is easily reduced compared to the geometrical width of these laterally tapered QWire structures. The model in Ref. [13] refers to calculations for square shaped quantum wires which is of course a very rough estimate. A precise model requires again the exact geometrical shape and composition which is not accurately enough known. The degree of polarization is relatively weak compared to other systems. This may partly be related to the surface orientation dependent valence band mixing resulting in a polarization perpendicular to the wires.

### 4.5 Conclusion

In conclusion, we have investigated the optical properties of stacked InGaAs sidewall quantum wires (QWires) with quaternary InGaAsP barriers grown on shallow-patterned InP (311)A substrates by chemical beam epitaxy (CBE). The temperature dependent integrated photoluminescence (PL) intensity indicated efficient carrier transfer from the adjacent quantum wells (QWells) into the QWires at low temperature and thermally activated repopulation of the QWells at higher temperature. The dependence of the PL
Optical Properties of Stacked Sidewall Quantum Wires

peak energy on temperature showed negligible localization of carriers along the QWires, indicating high uniformity in size and composition. Power dependent PL revealed strong broadening and high-energy shift of the QWire PL due to enhanced state filling in the QWires compared to that in the QWells. Pronounced linear polarization anisotropy of the PL from the QWires verified the lateral quantum confinement of carriers. Hence, excellent optical quality of the sidewall QWire structures is demonstrated with PL peak wavelength at room temperature at 1.55 μm required for applications in fiber-based optical telecommunication systems. Excitonic effects certainly play a role in the quantum wires, though they become not obvious in the experiments discussed here. Experiments like absorption and PLE measurements would reveal them, which will be a topic of further investigations.

Bibliography

Chapter 5

Sidewall Quantum Dots

5.1 Introduction

In this chapter we report the growth and optical properties of highly strained InAs/InGaAsP sidewall QDs on shallow-patterned InP (311)A. Larger and more symmetric InAs QDs are formed at the fast-growing [01-1]-oriented mesa sidewall compared to the shallower, dash-like QDs, elongated along [-233], in the planar areas. With increasing the sample temperature, the photoluminescence (PL) intensity of the sidewall QDs rises with respect to that of the quantum dashes in the planar areas due to thermally activated carrier transfer, leading to well-distinguishable emission in the temperature range around 80 K. As a function of excitation power density, the emission from the sidewall QDs reveals a large high-energy shift due to screening of the internal piezoelectric field by photogenerated carriers. Strikingly, the linear polarization of the PL from the sidewall QDs along [01-1] is reversed compared to that of the PL from the quantum dashes in the planar areas, polarized along [-233], which is attributed to the more symmetric shape and possible non-uniform strain in the growth plane perpendicular to the sidewall in these sidewall QDs formed on shallow-patterned InP (311)A.

5.2 Experiment

The InAs sidewall QDs were grown by chemical beam epitaxy (CBE) on a shallow-patterned InP (311)A substrate. The substrate pattern consisted of [01-1] oriented mesa stripes with 2 µm width, 4 µm pitch, and ∼ 30 nm height. The layer structure commenced with a 20 nm InP plus 20 nm lattice-matched In_{0.73}Ga_{0.27}As_{0.59}P_{0.41} buffer with bandgap

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This chapter is based on the paper J. Appl. Phys., 100:063505, 2006.
at 1.3 µm. The buffer layer was followed by 2.5 – 3.2 MLs InAs for QD formation in different samples, capped by 50 nm In$_{0.75}$Ga$_{0.27}$As$_{0.50}$P$_{0.41}$ after 5 seconds growth interruption, and a second 2.5 – 3.2 MLs InAs QD layer on top for structural analysis by atomic force microscopy (AFM) in air. The growth temperature was 500 °C and the growth rates were 0.40 ML/s for InAs and 0.52 ML/s for InGaAsP. The PL measurements of the sample presented here with 2.5 MLs InAs for QD formation were performed as described in the previous chapter.

5.3 Results and discussion

Figure 5.1 shows the AFM image of the surface morphology of the top InAs QD layer in the vicinity of the fast-growing mesa sidewall. The scan field is 1 × 1 µm$^2$ and the full height contrast is 10 nm. In the planar areas, the typical dash-like surface morphology is found, which is due to strain induced growth instability during deposition of InAs on InP (311)A [1] or (In,Ga)As on GaAs (311)A [2–4]. The dashes are elongated along [-233]. At the mesa sidewall, on the other hand, larger and higher InAs QDs are formed with a more symmetric shape. On planar substrates, nucleation of larger InAs QDs on top of the dashes occurs for deposition of InAs above 4 MLs [1]. This confirms the strong selective In adatom migration towards the fast-growing mesa sidewall on the shallow patterned InP (311)A substrate. No large QDs are observed at the opposite slow-growing mesa sidewall, which is solely covered by small dashes and dots.

The temperature dependent PL spectra from the mesa-patterned areas between 5 and 140 K are shown in Fig. 5.2. The excitation power density is 10 W/cm$^2$. At low temperature, only the PL from the quantum dashes in the planar areas is observed. With increase of the temperature a clear peak from the InAs QDs at the fast-growing mesa sidewall arises, which is red-shifted by 50 meV with respect to the PL peak from the quantum dashes. The spatial origin of the emission of the sidewall QDs is confirmed by the micro-PL spectra taken at 80 K from a single fast-growing sidewall of a wide mesa stripe and from an unpatterned, planar area, shown in the inset. No distinct change of the PL spectrum compared to that in the planar areas is observed at the opposite slow-growing sidewall. The relative increase with temperature of the emission of the sidewall QDs compared to that of the quantum dashes in the adjacent planar areas indicates thermally activated carrier transfer from the shallower quantum dashes with higher bandgap energy to the larger sidewall QDs with lower bandgap energy. This leads to strong and well-separated PL peaks around 80 K before the overall intensity drops due to thermal activation of carriers into the InGaAsP barriers.

Figure 5.3 shows the normalized excitation power density dependent PL spectra from the mesa-patterned areas taken between 1 and 100 W/cm$^2$ at the temperature of 80 K. A clear high-energy shift of the PL spectrum of the sidewall QDs and quantum dashes in the planar areas is observed with increase of the excitation power density. The high-energy
Figure 5.1: AFM image of the sidewall QDs and quantum dashes in the vicinity of the fast-growing mesa sidewall on shallow-patterned InP (311)A substrate. The scan field is 1 × 1 µm² and the full height contrast is 10 nm.

The high-energy shift of the PL spectra of the sidewall QDs and quantum dashes with excitation power density includes the PL peaks and the low- and high-energy sides, while the linewidths rather reveal a slight decrease in the excitation power density range under investigation. Hence, for these highly strained sidewall QDs and quantum dashes, the high-energy shift of the PL spectra as a function of excitation power density is attributed to piezoelectric effects present in strained nanostructures on non-(100)-oriented substrates [5–7].

Upon screening of the internal piezoelectric field by photogenerated carriers, the optical bandgap shifts to higher energies resulting in a blueshift of the whole PL spectrum. The linewidth of the PL spectrum remains unchanged or even reduces due to a shift of the wavefunction moduli away from the interfaces, reducing the influence of structural imperfections and size fluctuations. This is in contrast to the PL spectra of the weakly strained InGaAs quantum wires [8], exhibiting a high-energy shift and broadening with increase of the excitation power density due to state filling. In the case of state filling, the low-energy side of the PL spectrum remains unchanged or even shifts to lower energies.
Figure 5.2: Temperature dependent PL spectra of the sidewall QDs and quantum dashes in the mesa-patterned area. The excitation power density is 10 W/cm$^2$. Micro-PL spectra at 80 K from the single fast-growing sidewall of a wide mesa stripe and from an unpatterned planar area are shown in the inset.

due to Coulomb interactions, and the PL spectrum broadens or develops excited state emission at the high-energy side. For the same lattice mismatch, i.e. strain, the energy reduction of the optical bandgap due to the vertical and lateral internal piezoelectric field is larger for the larger sidewall QDs compared to that for the shallower quantum dashes as the total change in potential energy across the QDs is directly proportional to the size [9]. Hence, the high-energy shift of the PL spectrum with excitation power density due to screening of the internal piezoelectric field is much larger for the sidewall QDs than for the quantum dashes in the planar areas.

In Fig. 5.4 the linear polarization dependent PL spectra taken at 80 K from (a) an unpatterned, planar area and (b) the mesa-patterned area are depicted. The excitation power density is 10 W/cm$^2$. The PL from the quantum dashes is polarized along [-233] in accordance with lateral quantum confinement in the presence of the asymmetric,
Figure 5.3: Excitation power density dependent PL spectra at 80 K of the sidewall QDs and quantum dashes in the mesa-patterned area. The lower panels show the PL peaks at magnified scale.

The degree of linear polarization at the PL peak position, \( \frac{I_{[−233]}− I_{[01−1]}}{I_{[−233]}+ I_{[01−1]}} \), is 0.17 both, in the planar area and in the patterned area, indicating that the pattern does not affect the polarization properties of the emission from the quantum dashes. Strikingly, the degree of linear polarization of the PL from the sidewall QDs is always reduced in the different samples with varying In amount and even reversed for the sidewall QDs shown in Fig. 5.4. The degree of linear polarization at the PL peak position along [01-1] is - 0.16. The polar diagrams of the degree of linear polarization at the PL peak position of the sidewall QDs and quantum dashes are shown in Fig. 5.4 (c), which are well fitted by the formula

\[
I = A \sin(\theta)^2 + B \cos(\theta)^2,
\]

with A and B fitted to the PL intensities measured along the two perpendicular directions.

As for the sidewall quantum wires, also revealing linear polarization of the PL along [01-1] due to quantum confinement [8], electromagnetic (grating) effects [10] from the etched mesas are excluded due to the shallow height and the fact that they would affect
the polarization of the emission from the sidewall QDs and quantum dashes similarly. Therefore, the linear polarization of the PL from the sidewall QDs along [01-1] is attributed to quantum confinement in the more symmetric QDs and non-uniform triaxial strain distribution in the growth plane perpendicular to the sidewall [11] in those sidewall QDs formed on shallow-patterned InP (311)A substrates. For a quantitative description precise knowledge of the quantum dot composition, shape, strain state is required, which is particularly difficult to assess for such complex structures.

5.4 Conclusion

Growth and optical properties of highly strained InAs quantum dots (QDs) embedded in InGaAsP at the fast-growing [01-1] mesa sidewall on shallow-patterned InP (311)A substrates by chemical beam epitaxy have been reported. Temperature dependent photoluminescence revealed efficient carrier transfer from the adjacent dash-like QDs in the planar areas to the larger sidewall QDs, resulting in well-separated emission around 80 K. The large high-energy shift of the PL from the sidewall QDs as a function of excitation power density was attributed to internal piezoelectric effects. The linear polarization of the PL from the sidewall QDs is reversed compared to that of the quantum dashes in the planar areas due to the more symmetric shape and non-uniform strain distribution in the growth plane in the sidewall QDs. The distinct carrier transfer, enhanced optical nonlinearity due to internal piezoelectric effects, and polarization behavior make these sidewall QDs on shallow-patterned InP (311)A substrates interesting candidates for further basic physics studies and applications.
Figure 5.4: Linear polarization dependent PL spectra at 80 K (a) of the quantum dashes in an unpatterned, planar area and (b) of the sidewall QDs and quantum dashes in the mesa-patterned area. The excitation power density is 10 W/cm². (c) Polar diagram of the degree of linear polarization at 80 K at the PL peak position of the sidewall QDs and quantum dashes in the mesa-patterned area.
Bibliography


Chapter 6

Selective Area Growth for Lateral Wavelength Control

6.1 Introduction

In the preceding chapters, we studied the selective growth on shallow patterned substrates by CBE, while in this and the next chapter, an alternative technique, selective area growth (SAG) by MOVPE will be employed as a powerful tool to achieve lateral positioning and wavelength control of quantum dots.

Selective-area metalorganic vapor-phase epitaxy (SA MOVPE) is widely used for the monolithic integration of devices in a single growth step. It is based on lateral transport of the precursors from non-growing dielectric masked areas through vapor-phase and surface diffusion to unmasked areas, leading to local growth rate enhancement determined by the ratio of mask width to opening \[1–4\]. For bulk layers the growth rate enhancement has been intensively studied by measuring thickness and composition, directly related to the diffusion lengths and surface reactivities of the precursors \[5\]. Applied to quantum structures, the growth rate enhancement allows lateral tuning of the bandgap energy through the quantum size effect which has been successfully demonstrated for quantum wells (QWs) \[6, 7\] and quantum dots (QDs) \[8, 9\]. For applications in photonic devices operating in the technologically important 1.55 μm telecom wavelength region, however, the lateral wavelength control of QDs remains a challenge.

We report lateral wavelength control of InAs/InGaAsP/InP (100) QDs in the 1.55 μm wavelength region by combining SA MOVPE with the insertion of ultrathin GaAs interlayers underneath the QDs. As a function of the GaAs interlayer thickness, the QD

\[\text{This chapter is based on the paper J. Appl. Phys., 100:113512, 2006.}\]
emission wavelength is reduced into the 1.55 μm region \[10, 11\] while the lateral growth rate enhancement of InAs in SA MOVPE increases the QD emission wavelength. Atomic force microscopy (AFM) and micro-photoluminescence (micro-PL) reveal two regimes. For small InAs supply [2 monolayers (MLs) InAs together with 1 ML GaAs], a wide wavelength tuning range of 110 nm from 1450 to 1560 nm is obtained together with an increase of the QD height and density, indicating the evolution of QDs as a function of InAs growth rate enhancement. For larger InAs supply [3 MLs InAs together with 1.5 MLs GaAs], a much smaller tuning range of 25 nm from 1460 to 1485 nm is observed due to saturation of QD formation, supported by the increasing GaAs interlayer thickness. These two regimes enable complementary applications where either wide wavelength tuning or wavelength stability of QDs is beneficial in SA MOVPE.

6.2 Experiment

On the InP (100) substrates, mis-oriented by 2° towards (110), 100 nm SiNx was deposited by plasma-enhanced chemical-vapor deposition (PECVD) and patterned by conventional photolithography and reactive ion etching (RIE). A scheme of the 2 mm long triangular mask with maximum width of 150 μm and 10 μm wide open stripe along [011] is shown in Fig. 6.1 (a). The effect of the (local) mask width can be analyzed by studying the growth surface as a function of direction along the 2 mm long triangular mask. After cleaning in oxygen plasma and diluted phosphoric acid, the masked substrates were loaded into the MOVPE reactor. Trimethyl-indium (TMI), trimethyl-gallium (TMG), tertiarybutylarsine (TBA), and tertiarybutyl-phosphine (TBP) were used as precursors. The reactor pressure was 100 mbar. Growth commenced with 20 nm InP and 20 nm lattice-matched Q1.25 InGaAsP, which is a standard waveguide core material in photonic devices, at 580 °C before the substrate temperature was lowered to 500 °C for deposition of the GaAs interlayer and InAs QDs. The InAs (GaAs) supply was 2 (1) MLs and 3 (1.5) MLs in different samples. The TBA flow rate for InAs QD formation was 1 sccm. \[10\] The InAs QDs were capped by 20 nm InGaAsP (λQ = 1.25 μm; Q1.25), followed by 20 nm InP and a second 20 nm InGaAsP layer on which growth of the GaAs interlayer and InAs QDs was repeated for structural analysis by AFM. The growth rates were 0.75 ML/s for InAs and 0.21 ML/s for GaAs at 500 °C. The optical properties were assessed by micro-PL with a spatial resolution of 2–3 μm using the 632.8 nm line of a He-Ne laser with power of 10 μW as excitation source. The PL was dispersed by a 1-m single monochromator and detected by a cooled InGaAs charge-coupled device with detection limit at 1.6 μm. The growth rate enhancement was measured by a surface profiler (Tencor 10). Growth rate enhancement, AFM, and PL measurements were taken from the center of the 10 μm wide open stripe. Hence, mainly the growth rate enhancement effects related to vapor-phase diffusion are addressed, rather than those due to surface diffusion, leading to additional growth rate enhancement close to the mask edge, decaying on a μm length scale.

In our laboratory, the layers are grown in an AIX200/4 MOVPE reactor. The typical
growth temperature and reactor pressure are 585 °C and 100 mbar, respectively. The single wafer is positioned on a susceptor which consists of a graphite plate rotating in a graphite stator by means of gas foil rotation. The susceptor is heated by means of halogen lamps. The carrier gas is hydrogen. The precursor materials are kept in steel bubblers at defined temperatures. The concentration of precursor materials in the reactor and, hence, the growth rate is dependent on the source flow rate, the precursor vapor pressure, the total flow rate through the reactor, and the reactor pressure.

The following expressions are used to calculate the precursor concentrations in the reactor.

\[ \log(P_{\text{vapor}}) = A - B/T, \]

where A and B are constants depending on the precursor.

\[ P_{\text{reactor}}^{\text{partial}} = \frac{P_{\text{vapor}}}{(P_{\text{bubbler}} - P_{\text{vapor}}) \cdot \Phi_{\text{source}} / \Phi_{\text{total}} \cdot P_{\text{reactor}}}, \]

where \( \Phi \) is the flow rate.

In the table below some typical V/III ratios are given for different materials grown at 585 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>V/III ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP</td>
<td>41</td>
</tr>
<tr>
<td>Q1.25</td>
<td>33</td>
</tr>
<tr>
<td>Q1.5</td>
<td>31</td>
</tr>
<tr>
<td>InGaAs</td>
<td>43</td>
</tr>
</tbody>
</table>

Table 6.1: Typical V/III ratio at 585 °C used in our lab.

In MOVPE the partial pressures for TMI and TBP are kept constant in the reactor. For growth of quaternary layers TMG and TBA are added. The typical growth temperature is 585 °C. The longer the wavelength the more TMG and TBA need to be added. InAs QDs are grown at a lower reactor temperature of 500 °C. Typical InAs thicknesses are 2.5 – 4.5 monolayers (MLs). For QD wavelength tuning, GaAs interlayers are grown before the QDs with thicknesses between 0.8 and 3 monolayers. The Q1.25 barrier layers of the QDs are also grown at 500 °C to avoid annealing of the QDs at the standard growth temperature of 585 °C. At 500 °C the growth of Q1.25 is critical because the dissociation of TMG is kinetically controlled. If the temperature is decreased from 585 °C to 500 °C the TMG flow has to be increased from typically 3.5 sccm to 20 – 40 sccm to keep the same composition. In the kinetically controlled dissociation regime the growth rate is exponentially dependent on the wafer temperature. Consequently, very small temperature variations can give rise to large Q1.25 composition changes.
6.3 Results and discussion

6.3.1 Growth rate enhancement

Figure 6.1 (b) depicts the growth rate enhancement factor within the 10 µm wide open stripe as a function of the mask width determined by measuring the layer thickness. The growth is locally enhanced by the process described in § 2.4. The growth rate enhancement factor linearly scales with the mask width. Note that the growth rate enhancement is unity only after a few micrometer outside the masked area. In different experiments no significant dependence of the growth rate enhancement on the orientation of the mask is observed. For mask widths larger than 80 µm strong roughening of the surface morphology occurs. This indicates the onset of large compositional changes in the Q1.25 InGaAsP layer due to different diffusion lengths and surface reactivities of the group-III precursors (the group-V precursor supply is assumed to be not affected by the mask [5]) although, in the case of TMI and TMG, the growth rate enhancement of InAs is only slightly larger compared to that of GaAs [12]. For the analysis of the structural and optical properties of the InAs QDs we focus on mask widths less than 80 µm.

6.3.2 QDs formed by small InAs supply

Figure 6.2 shows the AFM images of the QDs formed by 2 MLs InAs and 1 ML GaAs interlayer in unmasked areas for different mask widths. This combination of InAs and GaAs supply is chosen to shift the QD emission wavelength (see Fig. 6.3) in the 1.55 µm region [10, 11]. Without GaAs interlayer, the QD emission wavelength is beyond 1.6 µm due to As/P exchange during InAs growth producing too large QDs. Hence, the role of the GaAs interlayer is to suppress As/P exchange, continuously reducing the QD height and emission wavelength as a function of GaAs thickness. With increasing mask width, i.e. growth rate enhancement, the average QD height increases from 3.5 to 5.5 nm and the QD density increases from $1 \times 10^{10}$ cm$^{-2}$ in unmasked areas to $4 \times 10^{10}$ cm$^{-2}$ for 80 µm mask width. This reveals strong evolution of the QD morphology as a function of InAs amount from underdeveloped QDs in unmasked areas to fully developed QDs in the masked areas.

The evolution of the QD morphology results in a strong shift of the PL spectra to longer wavelengths with increasing mask width, as shown in Fig. 6.3. The red shift of the PL peak emission wavelength is as large as 110 nm, from 1450 to 1560 nm, for the mask width of 60 µm. The peak at the short wavelength side, most evident for small mask widths, is attributed to emission from the wetting layer, which is expected to be most pronounced for low QD density. Excited state emission is excluded since the intensity ratio changes only marginally with excitation power. The PL intensity of the QDs drops by a factor of three when the mask width increases to 60 µm. This is attributed to defects formed due to increasing strain accumulation in the InAs QDs and GaAs interlayer, similar to unmasked areas where a decrease of the PL efficiency occurs for InAs supply above 4
ML and GaAs interlayer thickness larger than 2 MLs [10, 11], and/or reduced quality of the Q1.25 InGaAsP barrier layers due to compositional changes. Comparable wavelength shifts can be achieved for quantum wells, depending on the thickness in unmasked areas, since the growth rate enhancement is solely related to the mask design.

6.3.3 QDs formed by larger InAs supply

The AFM images for different mask widths of the InAs QDs formed by 3 MLs InAs and 1.5 MLs GaAs interlayer in unmasked areas are shown in Fig. 6.4. This combination of InAs and GaAs supply is chosen to obtain a similar QD peak emission wavelength in the unmasked areas for comparison (see Fig. 6.5). Independent on the mask width, the QDs are well developed, and the average QD height of 3.6 – 3.8 nm and density of $3 – 4.5 \times 10^{10}$ cm$^{-2}$ merely change. This indicates saturation of the QD formation with a self-limiting QD size in all areas which is reflected in a relatively stable PL peak emission wavelength as a function of mask width, shown in Fig. 6.5. The PL peak emission wavelength increases
Figure 6.2: AFM images of the 2 MLs InAs QDs with 1 ML GaAs interlayer for mask widths of (a) 0, (b) 10, (c) 20, (d) 40, (e) 60, and (f) 80 µm. The height contrast is 10 nm.

by only 25 nm, from 1460 to 1485 nm, for 60 µm mask width. A comparison of the PL peak emission wavelength shift as a function of mask width is shown in Fig. 6.6 for the QDs formed by 2 and 3 MLs InAs in unmasked areas. Also for the 3 MLs InAs QDs the PL intensity decreases by a factor of three for 60 µm mask width.

The stability of the QD morphology and emission wavelength in the regime of saturated QDs is supported by the increase of the GaAs interlayer thickness, compensating the QD height and wavelength increase with InAs amount for increasing mask width. Increasing the InAs supply from 3 to 3.5 MLs on unmasked substrates results in a slight QD height increase and PL red shift of 20 nm, independent on the GaAs interlayer thickness [10, 11]. On the masked substrate, the corresponding growth rate enhancement of 1.17 assumed for InAs produces a reduced PL red shift of only 12 nm, indicating the effect of the simultaneously increasing GaAs interlayer thickness. However, the growth rate en-
hancement of InAs is certainly larger than that of GaAs which is demonstrated by the fact that a thickness increase of 1.17 of the GaAs interlayer on the unmasked substrate produces a PL blue shift of 31 nm [10, 11]. Unfortunately, there is no reference without GaAs interlayer since InAs quantum dashes are formed for submonolayer GaAs coverage. For the QDs formed by 2 MLs InAs on the masked substrate the effect of increasing GaAs interlayer thickness is not visible due to the large wavelength shift upon QD evolution with increasing InAs amount. In the saturated regime the QD emission wavelength is stabilized by the interplay between increasing InAs supply and GaAs interlayer thickness.

6.4 Conclusion

In conclusion, we have investigated the lateral wavelength control of InAs/InGaAsP/InP (100) QDs by SA MOVPE. Through the combination of ultra-thin GaAs interlayers beneath the QDs with proper dielectric mask design the technologically important 1.55 μm wavelength region is covered. Micro-PL and AFM reveal a wide wavelength tuning range of 110 nm from 1450 to 1560 nm for small InAs supply [2 MLs InAs together with 1 ML GaAs] together with a QD height and density increase due to the evolution of QDs as a function of growth rate enhancement. For larger InAs supply [3 MLs InAs together with

Figure 6.3: Normalized micro-PL spectra taken at 10 K of the 2 MLs InAs QDs with 1 ML GaAs interlayer for different mask widths.
Figure 6.4: AFM images of the 3 MLs InAs QDs with 1.5 MLs GaAs interlayer for mask widths of (a) 0, (b) 20, and (c) 40 µm. The height contrast is 10 nm.

1.5 MLs GaAs], a much smaller tuning range of 25 nm from 1460 to 1485 nm is obtained due to saturation of QD formation and increasing GaAs interlayer thickness. Complementary applications are offered by the two regimes allowing either wide wavelength tuning or wavelength stability in SA MOVPE of InAs/InP QDs in the 1.55 µm telecom wavelength region for integrated photonic devices.
Figure 6.5: Normalized micro-PL spectra taken at 10 K of the 3 MLs InAs QDs with 1.5 MLs GaAs interlayer for different mask widths.

Figure 6.6: PL peak emission wavelength at 10 K of the 2 and 3 MLs InAs QDs as a function of mask width.
Bibliography


Chapter 7

Pyramid Formation, Position and Number Control of Quantum Dots

7.1 Introduction

Selective growth has been studied for various cases, shown in Fig. 7.1, including surface orientation dependent growth, planar selective area growth, embedded selective area growth, and growth on patterned substrates. In this thesis, most of these cases are explored for the lateral position and wavelength control of quantum wires and quantum dots. In Chapter 2, we introduced selective area growth (SAG) by MOVPE and CBE, which was applied in the last chapter to the lateral wavelength control of quantum dots in the 1.55 µm region. There, some position/area control of QDs is possible as well [1, 2] but the main emphasis is the control of the emission wavelength [3]. In this chapter, by exploring SAG in square shaped openings, precise position and number control of quantum dots is demonstrated.
SA MOVPE in square shaped openings produces pyramids with well defined facets which serve as templates for the area selective growth of quantum dots [4]. After depositing a thin dielectric mask directly on the substrate, patterning is performed by conventional photolithography and etching (wet chemical or RIE). For a proper mask design, i.e. mask widths smaller than the gas phase diffusion length of the order of 100 μm, growth takes place selectively in the square open areas while no material is deposited on the mask. Therefore, pyramidal structures and QDs can be locally grown within very small areas of micron or submicron dimensions. When the first growth is accomplished, the mask layer can be removed by RIE and regrowth can be carried out to planarize the surface as a step towards active-passive device integration at submicron length scales. Importantly, the size shrinking evolution of the pyramids leads to top dimensions reducing from micron to sub-micron length scales, which allows the use of conventional photolithography for mask patterning, avoiding the long writing times of electron-beam lithography to achieve sub-micrometer scale templates for quantum dot formation.

Quantum dots are selectively deposited on top of the truncated pyramids at different growth stages, i.e. dimensions of the top areas. The location, number, and emission wavelength of the quantum dots are therefore selectively controlled [5, 6]. For the InAs/InGaAsP/InP quantum dots emitting in the 1.55 μm region this is promising for device applications such as single photon sources for fiber based quantum communication systems [7]. Moreover, after regrowth, passive waveguides or photonic crystal cavities can be fabricated around the sub-micrometer active regions to fabricate novel opto-electronic integrated devices [8], such as low-power nanolasers. Combined with photonic crystal microcavities, even more interesting research areas based on the ultimate control of electrons and photons at the respective wavelength scales can be explored [9], as mentioned in Chapter 1.

7.2 Experiment

A 100 nm SiNx layer was deposited on the (100) InP substrates with 2 ° mis-orientation towards (110) by plasma enhanced chemical vapor deposition (PECVD) and then patterned by conventional photolithography and dry etching by RIE. The open areas are square shaped and aligned along [010] and [001]. The side lengths of the square shaped open areas are 1.5 ~ 2 μm and their center-to-center distance is 10 μm, which results in an area coverage of 2~4 %. The mask pattern is depicted schematically in Fig. 7.2. Before growth of the pyramids, the substrate was dipped in 1 % HF : 99 % H2O2 for a few seconds to remove any residues on the surface and then rinsed in de-ionized water. Prior to the second epitaxy (regrowth), the SiNx mask was stripped by oxygen plasma for 10 min with 300 Watt power and the generated surface oxide was removed by dipping in 10 % phosphorus acid for 2 min. Finally, the substrates were rinsed in DI water and blowed dry with pure N2 gas. For structural examination, the samples were stain-etched using 4.25 g KOH / 3 g K3Fe(CN)6 in 50 ml DI water for a few seconds to enhance the
cross-sectional SEM image contrast. The surface morphologies were characterized by top view AFM and SEM.

![Diagram of mask layout and growth directions]

Figure 7.2: Square shaped mask openings for pyramid formation by SA MOVPE

### 7.3 Results and discussion

#### 7.3.1 Pyramid formation

During selective area growth within the square shaped open areas, self-limiting side facets are formed due to the much higher growth rate of the (100) plane compared to that of the side facets. Here, we focus on the formation of InP pyramids, to avoid the complicated composition and strain variations occurring in selective area growth of InGaAsP. Also the growth parameter window for SA MOVPE of InP is assumed to be wider than that for InGaAsP. To systematically study the InP pyramid growth, a series of samples were grown to optimize the growth conditions. In principle, the mask layout, growth temperature, V/III ratio, growth rate, and the reactor pressure need to be adjusted to obtain good material selectivity with smooth facets and interface formation.

**Growth rate enhancement, material amount, and pyramid evolution**

Most important for the growth behavior is the effective deposition rate within the small open areas. A too large amount of material results in lateral growth on the masked areas (abnormal edge growth [10]), even if there is no direct deposition on the mask. In that
Results and discussion

Due to the strong growth rate enhancement in SA MOVPE, the material accumulation in the open areas is much larger compared to that in SA CBE, which is related to the different deposition mechanisms described in Chapter 2. Therefore, to control the growth rate within the small open areas it is very important to maintain a fixed mask layout. In our mask design, the ratio of open areas to masked areas is around 4%, as mentioned before, the total mask patterned area is 100 \( \mu m \times 100 \mu m \), i.e. smaller than the gas phase diffusion length \[11\], and the related growth rate enhancement is 30 \( \sim \) 60 times, which coincides roughly with the ratio of masked to open areas. This large growth rate enhancement makes the growth time control for the deposition of small material amounts critical. Moreover, due to the high growth rate enhancement, which even increases during pyramid formation due to the shrinking of the effective growth area (top area of the pyramids), the accurate control of the growth stage of the pyramids becomes critical. For practical flow rates in MOVPE this requires a response time for gas switching with 0.1 sec resolution, which however can be achieved.

In principle, both the \{110\} and \{111\} facet families can bound the pyramids. Figure 7.3 shows examples of pyramids formed by the two different types of side facets. Their baselines are 45° rotated with respect to each other and the angles between the sidewall facets and the substrate plane are distinctly different. Which of these pyramids are formed depends on the growth conditions. By reducing the material deposition under optimized growth conditions, the pyramids bound by four \{110\} side facets are obtained for the mask design with the square opening sides oriented along [010] and [001], used in this study. Due to the lower growth rate on the four \{110\} facets compared to that on the top (100) plane, the top (100) area shrinks very fast until the pyramid is completed (pinch-off). The different stages of pyramid evolution before pinch-off with top areas of 1 \( \mu m^2 \) to 0.01 \( \mu m^2 \) are shown in Fig. 7.4. However, due to the round corners of the photo-mask used for SiN\(_x\) patterning, four small \{111\} facets coexist with the \{110\} facets forming the pyramids, which results in complex pyramid shapes as seen in Fig. 7.3. This is not detrimental for forming sub-micrometer scale top areas for quantum dot deposition of high quality and optimizing the growth conditions for pyramid formation, but should be avoided by a better photo-mask quality for SiN\(_x\) patterning in future runs.

It should be mentioned, that with more material deposition, described in detail later, the pyramids bound by \{110\} side facets oriented along [010] and [001] develop into those oriented along [011] and [01-1] which are rotated by 45° relative to the square open areas. The four side facets belong then to the \{111\}A and \{111\}B families. Due to the faster growth rate of the \{111\}A than the \{111\}B facets \[12, 13\], the pyramids become elongated along the [011] direction. Therefore, the pyramids are less symmetric and exhibit concave or stair shaped defects resulting from lateral overgrowth on the mask. This is clearly seen in the topview SEM images in Fig. 7.5. Moreover, when the pyramid side facets are formed from \{111\} planes, no flat top is obtained since the initial pyramids (formed by
Figure 7.3: Sideview SEM images of pyramids formed by families of (a) \{110\} and (b) \{111\} side facets.

Figure 7.4: Topview AFM images of InP pyramids at different growth stages (a) initial (b) middle (c) final. The scan field is $3 \times 3 \mu m$, and the error signal of AFM feedback loop is shown in order to improve the visibility of the facets.

\{110\} side facets) have been already completed and the top (100) plane has varnished. Furthermore, with further material deposition, the pyramid top can become tip shaped again but, although the morphology is beautiful, there is significant lateral overgrowth on the masked area. Therefore, this type of pyramid is not suitable for the deposition of quantum dots on top. Thus, the only promising option to obtain smooth and symmetric pyramids with well-controlled (100) top areas is to exploit those bound by four \{110\} side facets which underlines the choice of our mask design with square shaped openings oriented along [010] and [001].

Cross-sectional SEM of the (011) or (01-1) cleavage planes is employed to get detailed information about the facet evolution during the material deposition. For the (110) cleavage plane, Fig. 2.3 in Chapter 2 depicts the various facets and their angles with respect to the (100) substrate plane. For example, when looking on the (110) cleavage plane, the \{111\} facet is inclined by an angle of 54.7°, while the \{110\} facet, projected on the cleavage plane, is inclined by an angle of 35.3° (the angle between the \{110\} facet and the
Results and discussion

Figure 7.5: Topview SEM images of InP pyramids with small material supply (a), and too much material supply (b) and (c)

(100) plane is 45°). Therefore, by measuring the angles between the facets and the (100) substrate plane, provided by the thin InAsP marker layers, we can distinguish {110} and {111} facets.

At the beginning of the growth, the top (100) plane exhibits the largest growth rate due to migration of adatoms from both the {111} facets and the {110} facets towards the top, leading to the development of the pyramid. After the pyramid bound by four {110} facets is completed and the top (100) plane has vanished, there is a competition for material deposition on the {110} or {111} facets. According to theory and various experimental observations [12], the growth rate is largest on the {111}A facets, decreases on the {110} facets, and is smallest on the {111}B facets. For the present growth conditions this also holds for InP growth. Therefore, after the pyramid bound by four {110} side facets is completed, growth on the {111}A and {110} facets and later on the {111}B facets takes place. This is reflected by the change of the angles between the side facets and the (100) substrate plane, provided by the marker layers, from 35.3° (4110 side facets) to 54.7° (4111 side facets), seen in Fig. 7.6. Finally, a new pyramid is formed with four {111} side facets. The orientation of the pyramid is, thus, rotated and the angle of the facets with respect to the (100) substrate plane is increased, as seen in the image of Fig. 7.3. As mentioned before, the pyramid is less symmetric due to the different growth rates on
the \{111\}A and \{111\}B planes, and the connection between the sidewall facets is rough. Figure 7.5 shows a comparison of the top view SEM images of the two types of pyramids bound by \{110\} (a) and \{111\} (b) side facets. After the top (100) plane has varnished lateral growth on the side facets commences, as seen in (b) and (c), which is undesired, causing difficulties in SiN\textsubscript{x} mask removal and regrowth, easily producing voids at the bottom of the pyramid.

![Image](image_url)

Figure 7.6: Cross-sectional SEM images of InP pyramids formed by proper amount of material (a) and too large amount of material (b).

**Growth temperature**

For our typical growth temperature of 585 °C, the surface and gas phase diffusion is not high enough, leading to the polycrystalline deposition on the mask and poor facet formation in the square open areas. With temperature increase to 650 °C, this is strongly improved, probably supported by enhanced desorption of material from the masked areas. Selective area growth is commonly performed at higher temperatures between 610 and 650 °C [13]. Further increase of the growth temperature leads to strong desorption of phosphorous and, thus, the incorporation efficiency of In will be reduced, which causes poor InP deposition in the open areas.

**Reactor pressure**

Reducing the reactor pressure from 100 mbar to 50 mbar, which might improve the growth selectivity due to enhanced desorption from the masked areas, resulted merely in any change of the material quality, as shown in the SEM images in Fig. 7.7 for (a) 100 mbar and (b) 50 mbar reactor pressure, respectively. The growth temperature for these samples is 650 °C. Therefore reactor pressures of and below 100 mbar are sufficient to guarantee good growth selectivity compared to atmosphere pressure MOVPE. In Ref. [14], it is mentioned that the growth rate enhancement close to mask edges is strongly reduced.
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for low reactor pressure and rather extends over tens of micrometers into the open areas. Therefore, the long-range uniformity might be improved for low reactor pressures resulting from the corresponding increased gas phase diffusion length. Taking into account that the lower reactor pressure may increase the surface migration length of adatoms as well, we continue with 50 mbar reactor pressure for the following samples.

![SEM images](image)

Figure 7.7: SEM images of InP pyramid arrays grown with different reactor pressure, (a) 50 mbar and (b) 100 mbar.

TBP flux rate

After optimizing the selectivity of material deposition between open areas and masked areas, further optimization of the facet formation during pyramid growth is required. In our case, facet formation is primarily related to the surface migration of adatoms, since the dimensions of the open areas, smaller than 2 µm, are comparable to the surface migration length of adatoms and much smaller than the diffusion length in the gas phase. Figure 7.8 shows the cross-sectional SEM micrographs of InP pyramids with three InAsP marker layers indicating the evolution of the InP pyramids during growth and reflecting the material quality through interface smoothness.

In principle, decreasing the TBP flux rate may result in enhanced surface migration of group III adatoms. Therefore, various TBP flux rates are adopted to optimize the pyramid formation with respect to smooth side facets and high growth rate on the top (100) plane. Figure 7.8 shows the cross-sectional SEM images of the InP pyramids cleaved close to the center grown under TBP flux rates of 250 (a), 125 (b), and 50 (c) sccm, respectively. The reactor pressure is 50 mbar and the growth temperature is 610 °C. For a TBP flux rate of 250 sccm, a very rough growth front, indicated by the InAsP marker layers, is observed with a concave depression present on the top. This reveals that the material accumulates at the corner between the side facets and the top plane, i.e. the migration length of the adatoms coming from the side facets is too small in order to reach the top plane and distribute uniformly. Only with more material deposition, when the top area
decreases, the depression is filled up, however, the reproducibility and controllability is low due to the large variations of the surface profile. For a reduction of the TBP flux rate to 125 sccm, the InAsP marker layers indicate improved facet formation during the pyramid evolution. The undulations of the profile are probably caused by the InAsP marker layers themselves due to the large lattice mismatch. Further reduction of the TBP flux rate to 50 sccm produces flat InAsP marker layers indicating that the migration length of the In adatom from the beginning of the growth is large enough in order to reach the top (100) surface and distribute uniformly, resulting in well developed and smooth sidewall facets. Reduction of the growth rate might be another parameter to increase the surface migration length of the In adatoms which is, however, not practical with our gas supply system.

Achievement of pyramid formation

The well-controlled pyramid evolution at different stages is revealed in the topview AFM images in Fig. 7.4. The scanned areas are $3 \times 3 \, \mu m$ for all images. Fig. 7.4 (a) shows the truncated pyramid with large top area. With increasing material deposition amount the top area is reduced from an intermediate stage as shown in 7.4 (b) to a top area with dimensions less than 400 nm, which is shown in 7.4 (c). Therefore, a well-defined template with submicron dimensions is realized by using conventional photolithography for the further deposition of low-dimensional quantum structures.

All the above described optimization of the pyramid formation is based on our fixed mask design and the strong growth rate enhancement in SA MOVPE. Changing the mask design will require re-optimization of the growth process which is a slight disadvantage of SA MOVPE where the growth rate enhancement arises from both surface migration and gas phase diffusion, in contrast to SA CBE. For our mask design, the optimized growth conditions for InP pyramid formation are a TBP flux rate of 50 sccm, a growth temperature of 650 °C and a total reactor pressure of 50 mbar. The InP pyramid is completed for a material supply of 13 nm in planar areas, revealing the high growth rate enhancement factor of $\sim 30$. For larger mask openings of 3 μm side lengths these growth conditions do not result in well-shaped pyramids confirming the relation between mask design and optimized growth conditions.

To further optimize the growth conditions for pyramid formation, reduction of the TMI flux rate to increase the adatom migration length on the sample surface is recommended, though difficult with our MOVPE system. In addition, the growth temperature might be further optimized in the range between 610 and 650 °C. Moreover, a better quality of the photo-mask for SiN$_x$ patterning with sharp corners will avoid formation of the small $\{111\}$ facets during the pyramid growth.
Figure 7.8: Cross-sectional SEM images of cleaved InP pyramids grown under a TBP flux rate of (a) 250 sccm, (b) 125 sccm, and (c) 50 sccm.
7.3.2 Quantum dot positioning

InAs QDs are deposited on top of the InP pyramids at different growth stages with dimensions of the top areas, seen in Fig. 7.4, of (a) 1.1 (b) 0.7, and (c) 0.4 µm respectively. According to our experience with QD formation on planar surfaces [15], the optimized growth temperature for quantum dots is 500 °C to suppress As/P exchange in addition to the suppression of As/P exchange by ultrathin GaAs interlayers. Therefore, after lowering the substrate temperature from 650 to 500 °C, a 0.05 ML GaAs interlayer and 0.1 ML InAs (referring to a growth rate enhancement factor of around 30 with respect to the growth on the planar substrate) were deposited, aiming at an effective 1.5 ML GaAs interlayer and 3.0 ML InAs quantum dots on the top area of the pyramids. These thicknesses are chosen to achieve a quantum dot emission wavelength in the 1.55 µm range with InP as barrier material. The morphologies of the quantum dots on top of the pyramids are shown in the AFM images in Fig. 7.9. The scanned areas are 3 × 3 µm. Deposition on the large top area results in more than hundred quantum dots, shown in (a). With slightly reduced top area (b), the number of quantum dots is decreased as well. When the dimensions of the top areas are reduced to submicron length scales, the quantum dot number is reduced from several hundred to several tens on the pyramid (c). These results confirm that the quantum dots are well grown within the selected areas with tunable number. Further adjustment of the growth conditions is anticipated to lead to formation of only a few or single quantum dots, which is the topic of future research.

Micro-PL measurements at low temperature were performed to study the optical properties of the quantum dots. For micro-PL, the quantum dots were covered by 10 nm InP (on the truncated pyramid) at 500 °C before the temperature was increased to 650 °C for completion of the pyramids. Corresponding to the different pyramid growth stages at which the quantum dots were deposited, a series of spectra is plotted in Fig. 7.10. When several hundred quantum dots are present on the large and medium top areas of the pyramid, the micro-PL spectra are relatively smooth and broad, with peak emission wavelength around 1450 nm in (a). This indicates that the ultra thin GaAs interlayer plays the same important role to prevent As/P exchange as on planar substrates to tune the quantum dot emission wavelength in the 1.55 µm range. For reduced top area (b), the emission wavelength of the quantum dots is red shifted to 1480 nm due to slightly larger QD dimensions originating from the larger growth rate enhancement. For the QDs deposited on the smallest top areas, the micro-PL spectra split into sharp peaks around 1500 nm indicating the emission from individual dots. On some pyramids, no emission around 1.5 µm is observed, but merely a single peak centered at 1230 nm is present which is attributed to the emission from the InAs wetting layer when the deposition amount is below the critical thickness for quantum dot formation due to non-uniformities of the growth rate. But on most pyramids position control of QDs is well-obtained and the number of the QDs is tuned through the dimensions of the top area of the pyramids, allowing the detection of the emission from single quantum dots which is promising for the realization of single photon sources in the 1.55 µm wavelength range.
7.3.3 Regrowth attempt

Towards the integration of such submicrometer scale active regions in photonic devices, the regrowth of a passive InGaAsP/InP waveguide around the InP pyramids is studied. After formation of the InP pyramids containing QDs the SiN$_x$ mask was completely removed in 10 % HF for 3 minutes (over etched) and then the samples were rinsed in DI water. Prior to the regrowth, the samples were cleaned in an oxygen plasma for 10 minutes with power of 300 Watt and the generated oxide layer was removed in 10 % phosphoric acid. This process was repeated for three times to assure a clean surface. The regrown structure consisted of a thin (150 nm) InP buffer layer, 500 nm Q1.25 InGaAsP, and 500 nm InP. Taking into account that the growth rate during regrowth will also be enhanced due to the presence of the pyramids, a reduced deposition amount is chosen. Different growth temperatures were applied to achieve good surface morphology and planarity of the waveguide structure around the pyramids.

During regrowth, the presence of the pyramids leads to a complicated growth mechanism between the pyramid facets and the substrate plane. For growth at 510 °C, the surface morphology is rough and the material accumulates around the pyramid base. When the growth temperature is increased to 585 °C, the material quality is improved, as shown in Fig. 7.11. The cross-sectional SEM image reveals a higher growth rate on the {110} sidewall facets than on the (001) surface. A growth rate enhancement factor of two is deduced from the SEM image. The large growth rate on the {110} facets might be suppressed through further increasing the substrate temperature and/or optimizing the group V flux rate. The rough morphology of quaternary layer still exists at the sidewall due to the In composition variation. The growth of quaternary does show a planarity process in contrast to that of InP. Significant optimization is required to apply this regrowth scheme for submicron scale integrated active photonic structures.

7.4 Conclusion

In conclusion, we have investigated position and number control of InAs quantum dots formed on selectively grown InP pyramids. For optimized growth conditions, InP pyramid can be fabricated bound by symmetric sidewall facets. The QDs are located in the top areas of the pyramids and their number is tuned by the dimensions of the top areas at different stages of the pyramid formation. Micro-photoluminescence reveals the emission spectra from individual QDs when their number is reduced. Embedding the active pyramid structure in passive waveguides has been attempted. This technique is promising for fabrication of single photon sources operating in the 1.55 µm region and the submicron scale active-passive photonic integration for novel low-power nanolasers.
Figure 7.9: Topview AFM images of quantum dots formed on top of the truncated pyramids with (a) large top area, (b) reduced top area, and (c) small top area. The scan field is $3 \times 3$ $\mu$m, and the error signal of AFM feedback loop is shown in order to improve the visibility of the facets.
Figure 7.10: Micro-PL spectra of QDs formed on top of truncated pyramids with (a) large top area, (b) reduced top area, and (c) small top area.
Figure 7.11: Cross-sectional SEM image of the regrown structure. The growth temperature is 585 °C.
Bibliography


Chapter 8

Summary

In this thesis epitaxial growth and analysis of the optical properties of semiconductor nanostructures, i.e. quantum wires (QWires) and quantum dots (QDs) in the InGaAsP/InP materials system with emphasis on the lateral ordering and positioning of such nanostructures are studied. This is the essential prerequisite for application of such nanostructures in future quantum functional devices operating in the technologically important 1.55 µm wavelength region.

(In,Ga)As sidewall QWires are realized by chemical beam epitaxy (CBE) along [01-1] mesa stripes on shallow-patterned InP (311)A substrates. The QWires exhibit strong lateral carrier confinement due to larger thickness and In composition compared to the adjacent quantum wells (QWells), as determined by cross-sectional scanning tunneling microscopy (X-STM) and micro-photoluminescence (micro-PL) spectroscopy. The PL of the (In,Ga)As QWires with InP and quaternary (Ga,In)(As,P) barriers reveals narrow line width, high efficiency, and large lateral carrier confinement energies of 60 – 70 meV. The QWires are stacked in growth direction with identical PL peak emission energy. The PL emission energy is not only controlled by the (In,Ga)As layer thickness but also by the patterned mesa height.

Stacked (In,Ga)As QWires with quaternary barriers exhibit room temperature PL emission at 1.55 µm in the technologically important wavelength region for telecommunication applications. Temperature dependent PL reveals efficient carrier transfer from the adjacent QWells into the QWires at low temperature, thermally activated repopulation of the QWells at higher temperature, and negligible localization of carriers along the QWires. Strong broadening of power dependent PL indicates enhanced state filling in the QWires compared to that in the QWells. Clear linear polarization of the PL from the QWires confirms the lateral quantum confinement of carriers.

Moreover, highly strained InAs QDs embedded in InGaAsP are formed at the fast-growing [01-1] mesa sidewall. Temperature dependent PL reveals efficient carrier transfer from the adjacent dash-like QDs in the planar areas to the larger sidewall QDs resulting
in well-distinguishable emission around 80 K. The large high-energy shift of the PL from
the sidewall QDs as a function of excitation power density is ascribed to the screening of
the internal piezoelectric field. The linear polarization of the PL from the sidewall QDs
is reversed compared to that of the quantum dashes in the planar areas due to the more
symmetric shape and possible non-uniform strain in the sidewall QDs.

Lateral wavelength control of InAs quantum dots (QDs) embedded in InGaAsP on
InP (100) substrates by selective-area metalorganic vapor-phase epitaxy (SA MOVPE)
is achieved. The technologically important 1.55 µm wavelength region is assessed by
the combination of ultra-thin GaAs interlayers beneath the QDs with proper SiNx mask design.
Atomic force microscopy and micro-PL reveal evolution of the QDs formed by 2 MLs InAs
as a function of growth rate enhancement with pronounced height and density increase,
resulting in a wide wavelength tuning range of 110 nm. Saturation of QD formation is
observed for 3 MLs InAs supply producing a much smaller tuning range of only 25 nm
which is supported by the increasing GaAs interlayer thickness. Hence, two regimes are
identified allowing either wide wavelength tuning or wavelength stability in SA MOVPE
of QDs in the 1.55 µm region offering complementary applications.

Positioning of InAs QDs on InP (100) substrates is obtained by SA MOVPE applying
mask patterns with square shaped openings. Selectively grown InP pyramids at different
growth stages serve as template for the positioning of InAs QDs with tunable number
depending on the size of the pyramid top areas. The QDs embedded in the InP pyramids
exhibit high PL efficiency and the emission from single QDs is revealed in micro-PL when
the number of QDs is reduced to several tens. Embedding the active InP pyramids in
passive InGaAsP/InP waveguides has been attempted. This technique is promising to
fabricate single photon sources operating in the 1.55 µm region.

The growth of lateral nanostructures on shallow-patterned (311)A substrates is based
on the preferential migration of adatoms from the mesa top and bottom to the mesa side-
wall. This process is highly reproducible, and the shallow patterns result in quasi-planar
growth making the material quality comparable to that obtained by growth on unpat-
terned substrates. The quasi-planar structures also simplify further processing needed
for device fabrication. QWire and QD structures are successfully achieved with excellent
material quality and optical properties at the sidewall area. However, the degree of the
selectivity and the lateral width of the sidewall area are not easy to control especially on
InP substrates, which can, however, be addressed by the layer design, mesa height, and
the pattern pitch.

In contrast to the growth on patterned substrates, selective area growth relies on the
interplay of gas phase diffusion and surface diffusion with the mask design and growth
rate enhancements are considerably less affected by the substrate orientation. Moreover,
the degree of growth rate enhancement or growth selectivity can be controlled by the
geometrical design of the mask pattern, which provides a flexible parameter for the design
and control of lateral nanostructures.
In this thesis, various techniques for the formation of lateral nanostructures based on the epitaxial growth on patterned (non-planar or masked) substrates combined with self-assembled growth techniques have been studied aiming at lateral position and wavelength control of quantum wires and quantum dots. Significant progress towards this goal has been achieved demonstrating the strength of combining alternative techniques for lateral nanostructure formation for the realization of quantum wires and quantum dots which may find applications in novel quantum effect devices.
Publications


neering on shallow-patterned substrates. In 14th International Conference on Molecular Beam Epitaxy, MBE 2006, Tokyo (Japan), Sept. 3-8, 2006.


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Resume

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List of Abbreviations

QW, QWell quantum well
QWR, QWire quantum wire
QD, QDot quantum dot
InGaAsP (Ga,In)(As,P)
MBE molecular beam epitaxy
MOVPE metal organic vapour phase epitaxy
CBE chemical beam epitaxy
RIE reactive ion etching
SAG (SAE) selective area growth (epitaxy)
AFM atomic force microscopy
X-STM cross-sectional scanning-tunneling microscopy
SEM scanning electron microscopy
PL photoluminescence
μ-PL micro-photoluminescence
TMI, TMIn trimethyl-indium
TEG, TEGa triethyl-gallium
TMG, TMGa trimethyl-gallium
TBA, TBAs tertiarybutyl-arsine
TBP tertiarybutyl-phosphine