1
Semiconductor Quantum Dots for Ultrafast Optoelectronics

1.1
The Role of Dimensionality in Semiconductor Materials

The history of semiconductor lasers has been punctuated by dramatic revolutions. Several proposals of injection semiconductor lasers were studied between the late 1950s and the early 1960s, and the first demonstrations of p–n junction GaAs lasers followed in 1962 [14]. Until the 1980s, only bulk materials were used in semiconductor devices. Originally, these were homostructure devices, functionalized by a doping profile including a p–n junction in the same material. However, these lasers exhibited very low efficiency due to high optical and electrical losses. At that time, pioneers such as Alferov and Kroemer independently proposed a laser construction known as the double heterostructure and involving an active layer of a semiconductor with a relatively narrow bandgap layer surrounded by two injector layers of more broadband material [15]. Such a design offers several crucial advantages. First, it efficiently localizes the charge carriers of both signs (electrons and holes) within the active layer, by creating a potential well for both types of carriers. This potential well also leads to the possibility of achieving carrier densities in the active layer exceeding the doping level of the injector layers (the superinjection effect); thus, low-doped injectors can be used and the optical losses are significantly decreased compared to those in early homostructure lasers, which were by necessity highly doped. Second, as narrowband materials tend to have a higher refractive index, the electronic confinement is accompanied by the *optical* confinement, with an epitaxially determined waveguide formed in the transverse direction (perpendicular to the plane of the epitaxial layers). In the simplest version of a double heterostructure, the active layer doubles as the waveguide core; most structures currently used, including quantum dot (QD) lasers, use a *separate confinement* arrangement whereby the relatively thin active layer is embedded in the broader *optical confinement layer* (made of a broader bandgap material to localize the carriers in the active layer), which, in its turn, is sandwiched between two cladding (p- and n-emitter) layers. These have a still broader bandgap and thus, importantly, a lower refractive index than that of the optical confinement layer to provide the optical confinement/waveguiding.

Ultrafast Lasers Based on Quantum Dot Structures: Physics and Devices.
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ISBN: 978-3-527-40928-0

The enhanced electronic and optical confinement (localization) in the double heterostructure drastically improved the operational characteristics of laser diodes, in particular the threshold current density (current per unit area) J_{th}, which decreased by as much as two orders of magnitude.

Another revolution followed when it was realized that the confinement of electrons to lower dimensional semiconductor structures translates into completely new optoelectronic properties, compared to bulk semiconductors. The obvious can therefore be asked: how small should this confinement be? To answer this question, one should recall the concept of the de Broglie wavelength of thermalized electrons λ_B, as shown in Equation 1.1:

$$\lambda_B = \frac{h}{p} = \frac{h}{\sqrt{2m^* E}}, \tag{1.1}$$

where h is Planck's constant, p is the electron momentum, m^* is the electron effective mass, and E is the energy.

In the case of III–V compound semiconductors (such as the AlGaAs and InGaAsP material systems), λ_B is typically on the order of tens of nanometers for carriers with typical thermal energies [16]. Therefore, if one of the dimensions of a semiconductor is comparable to, or less than λ_B, the electrons will be confined to two dimensions and so the energy–momentum relations will dramatically change because quantization effects start to take place in one of the dimensions. This is the case for charge carriers in a quantum well (QW) structure, which have been intensively studied since the 1970s and are now prevalent in semiconductor lasers and, to a lesser degree, in amplifiers.

The next stage in reducing dimensionality in a semiconductor active medium is the quantum wire (QWR), which is a one-dimensional confined structure in the sense that the carrier movement is free in one dimension and confined in two others. Quantum wires can be fabricated by direct lithographic methods, but possibly the most important one-dimensionally confined structure from the laser device perspective is the quantum dash (QDH) structure considered in more detail below.

Finally, a quantum dot is a nanostructure in which the electron and hole movement is confined in all the three dimensions. Quantum dots are thus tiny clusters of semiconductor material having all three dimensions of only a few nanometers.

The spatial confinement of the carriers in lower dimensional semiconductors leads to dramatically different energy–momentum relations in the directions of confinement, which results in completely new density of states, compared to the bulk case, as depicted in Figure 1.1.

As dimensionality decreases, the density of states is no longer continuous or quasi-continuous but becomes quantized. In the case of quantum dots, the charge carriers occupy only a restricted set of energy levels rather like the electrons in an atom, and for this reason, quantum dots are sometimes referred to as "artificial atoms." It is important to stress, however, that QDs actually contain hundreds of thousands of atoms.

For a given energy range, the number of carriers necessary to fill out these states reduces substantially as the dimensionality decreases, which implies that it becomes

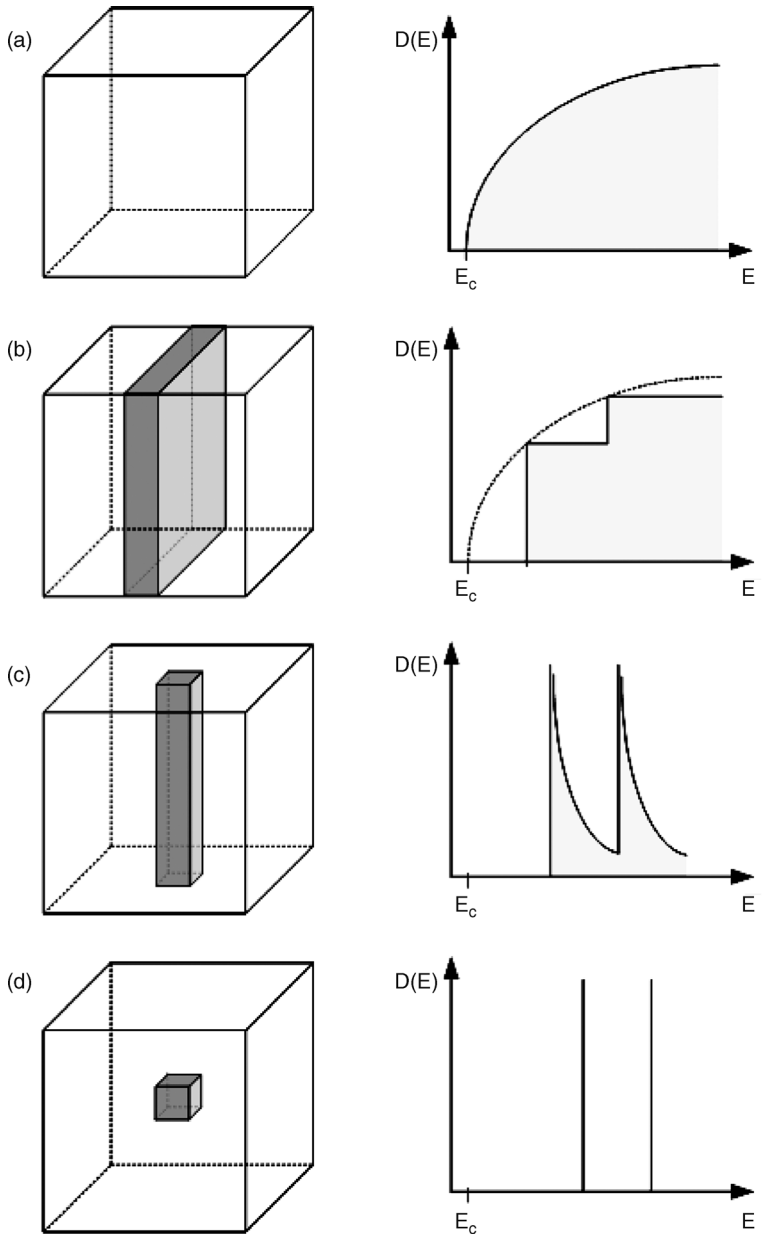

Figure 1.1 (*Right*) Schematic morphology and (*left*) density of states for charge carriers in semiconductor structures with different dimensionalities: (a) bulk, (b) quantum well, (c) quantum wire, and (d) quantum dot.

easier to achieve transparency and, eventually, the inversion of population needed to achieve optical gain and thus laser operation – with the resulting reduction of the threshold current density J_{th} of a laser. In fact, the reduction in J_{th} has been quite spectacular over the years, with sudden jumps whenever the dimensionality is decreased [15]. Low-dimensional lasers also exhibit reduced temperature sensitivity of J_{th}, and in the case of quantum dots, an infinite characteristic temperature has even been predicted.

The implications of a quantized density of states for QDs are immense and were identified as early as 1976 when a QD laser was first proposed [17]. A subsequent theoretical treatment was published in 1982 [18] in which it was predicted that the ideal three-dimensional localization of carriers would translate into a low-threshold, temperature-insensitive, and single-frequency laser. The latter two predictions relied, however, on the assumption of the dots being nearly identical and this having almost the same energy level separation (weak inhomogeneous broadening). While realization of such QD systems may yet become possible in future, all the dot structures grown so far have a significant size (and possibly composition) dispersion, leading to a significant inhomogeneous broadening of the emission line. Thus, some of the initial expectations from QD laser, such as the single-frequency lasing, had to be revised, while others, such as application for ultrafast optoelectronics, became more feasible. This will be discussed in more detail in Chapter 2, which will present a summary of quantum dot theory concentrating on the areas of interest to the subject of short pulse generation and amplification.

1.2 Material Systems Used

A variety of materials have been used in the past in the fabrication of quantum dots. In the following sections, we will describe the main QD material systems that have shown particular promise for ultrafast optoelectronic applications.

1.2.1 III–V Epitaxially Grown Quantum Dots

Since the pioneering work reported in 1985 [19], where the formation of InAs clusters in a GaAs matrix was demonstrated, a number of groups have synthesized and studied self-organized QD structures in a range of distinctive systems [20]. One of such groups of materials is based on III–V QDs, epitaxially grown on a semiconductor substrate. To date, the most promising results have been achieved through the spontaneous formation of three-dimensional islands during strained layer epitaxial growth – a process known as the Stranski–Krastanov mechanism. In this process, when a film is epitaxially grown over a substrate, the initial growth occurs layer by layer, but beyond a certain critical thickness, three-dimensional islands begin to form – the quantum dots. A continuous film, of quantum well thickness and usually assumed to have quantum well properties, lies underneath the dots and is called the

wetting layer. A crucial requirement of this technique is that the lattice constant of the deposited material is larger than that of the substrate, so that the additional strain leads to the formation of clusters. This is the case of an InAs film (lattice constant of 6.06 Å) on a GaAs substrate (lattice constant of 5.64 Å) or on an InP substrate (lattice constant of 5.87 Å). Many different systems can be grown using this technique and these are not limited to group III–V constituents.

Despite being an extremely complex process, the Stranski–Krastanov mode is now widely used in the self-assembly of quantum dots. Epitaxial quantum dot materials can be grown using molecular beam epitaxy (MBE) and metal organic chemical vapor deposition (MOCVD). These techniques have been extensively used in the past decades to grow QW materials and therefore the growth of QDs benefited immensely from well-established procedures. This aspect is also advantageous for commercialization, as manufacturers do not need to invest in new epitaxy equipment to fabricate these structures.

Stranski–Krastanov-grown quantum dots typically have a pyramidal shape, with a base of 15–20 nm and a height of the order of ∼5 nm (it is possible that after overgrowth, this shape is modified). At present, the densities of quantum dots lie typically between 10^9 and $10^{12}\,cm^{-2}$. The relatively sparse distribution of quantum dots results in a low value of gain. Thus, the levels of gain and optical confinement provided by a single layer of quantum dots may not be enough for the optimal performance of a laser. To circumvent this problem, quantum dot structures are routinely grown in stacks that allows an increase in the modal gain without increasing the internal optical mode loss [21]. Further optical confinement is enabled through the embedding of QD arrays within layers of higher refractive index and bandgap energy, therefore forming a heterostructure.

Figure 1.2a and b [22] shows a surface view of a system of self-organized QDs and a side view of a stack of three QD layers, respectively, to give an idea of dimensions, distances, and shapes of typical self-organized QDs in a practical device structure. In this case, the dot density in each layer is around $4 \times 10^{10}\,cm^{-2}$, with the lateral size of QDs of 15–18 nm. The apparent dot bases are almost square shaped and oriented along the ⟨100⟩ direction in the crystal, with a slight elongation along one of the ⟨110⟩

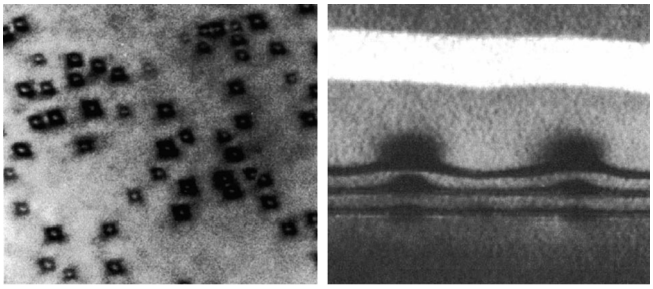

Figure 1.2 Scanning electron microscope image of a plan view (a) and side view (b) of a system of three-stacked QDs in a laser structure. Courtesy of D. Livshits, Innolume GmbH.

directions. Note also that the average size of the dots appears to increase from layer to layer, contributing to the inhomogeneous broadening as discussed below.

Materials based on InGaAs/InAs dots grown on a GaAs substrate have been investigated quite comprehensively in the past few years because their emission wavelengths can not only be tuned between 1.0 and 1.3 μm but can also be extended to 1.55 μm [20], through careful adjustment of the growth conditions. InGaAs/InAs QDs grown on InP substrate emit in the 1.4–1.9 μm wavelength range, thus enabling easy access to the optical communications band around 1.55 μm.

Epitaxially grown QD materials have been successfully deployed in the form of lasers, amplifiers, and saturable absorbers – and as such, they hold great promise for a complete optoelectronic integration of an array of distinct devices on the same wafer.

1.2.2
QD-Doped Glasses

QD-doped glasses represent the second key group of quantum dot materials that are of significant interest in ultrafast physics. These materials consist of semiconductor nanoparticles (such as PbS, PbSe, and CdTe) incorporated into a variety of transparent dielectric matrices, with excitonic absorption peaks in the spectral range of about 0.5–2.5 μm [23–25]. One of the main advantages of QD-doped glasses is that they are much cheaper and easier to produce than their epitaxially grown counterparts. QD-doped glasses have not yet realized their full potential as gain media in that efficient laser emission has not been observed to date. Moreover, they are not yet practical within the context of fabricated electrically injected devices. This material system is thus being investigated mainly as an absorber medium. QD-doped glasses have, in fact, been successfully used as ultrafast saturable absorbers and optical switches because they exhibit similar ultrafast properties to III–V QDs in heterostructures.

1.2.3
Quantum Dashes

Quantum dashes are often mentioned alongside quantum dots and are produced in a similar technological process, typically by growing InAs (notionally a few monolayers) on top of thin AlGaInAs/InP layers – such QDHs emit in the 1.55 μm wavelength band. However, the energy structure of quantum dashes is very different from those of quantum dots. Like QDs, QDHs have a vertical dimension of the order of 3–4 nm and a lateral dimension of 10–20 nm. However, unlike a QD, a QDH is elongated in the other lateral dimension, its typical length being on the order of fractions of a micron, which is considerably larger than the electron and hole de Broglie wavelengths. Therefore, two of the three components of the carrier wave vector in a QDH are quantized, but the third one is quasi-continuous, meaning that instead of discrete energy levels, like QDs, a single QDH has quasi-continuous energy bands for both electrons and holes, like bulk and QW materials, although the

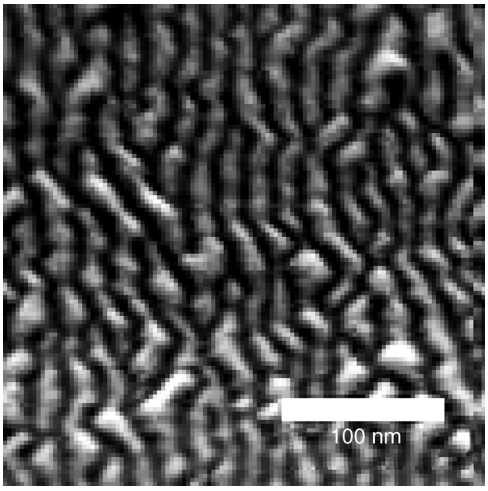

Figure 1.3 Scanning electron microscope image of a plan view of a sample of nonovergrown InAs quantum dashes. Reproduced with permission from Ref. [26].

density of states for electrons and holes has sharp peaks, reminiscent of the delta functions of QDs. In theoretical models, the properties of QDHs are quite well described [26] as similar to those of quantum wire assemblies with fluctuating transverse/lateral dimensions. This approach is not absolutely accurate because, unlike quantum wires, QDHs are self-assembled with a high density (hence there is a possibility of tunneling between them), and their geometry is more irregular than that of ideal quantum wires (an example is shown in Figure 1.3), but it has been shown in several papers that this irregularity does not significantly affect the QDH properties [26].

1.3
Quantum Dots: Distinctive Properties for Ultrafast Devices

1.3.1
Inhomogeneous Broadening

The main motivation behind the idea of a QD laser was to conceive a design for a low-threshold, single-frequency, and temperature-insensitive laser given the quantum nature of the density of states. Interestingly, practical devices exhibit the predicted outstandingly low thresholds [27, 28], but the spectral bandwidths of such lasers are significantly broader than those of conventional quantum well lasers [29]. This characteristic is attributable to *inhomogeneous broadening* with its dependence on the dot size distributions. Indeed, because of their self-organized growth, QDs exhibit a Gaussian distribution of sizes, with a corresponding, nearly Gaussian in the first approximation, distribution of emission frequencies. Also, fluctuations in the

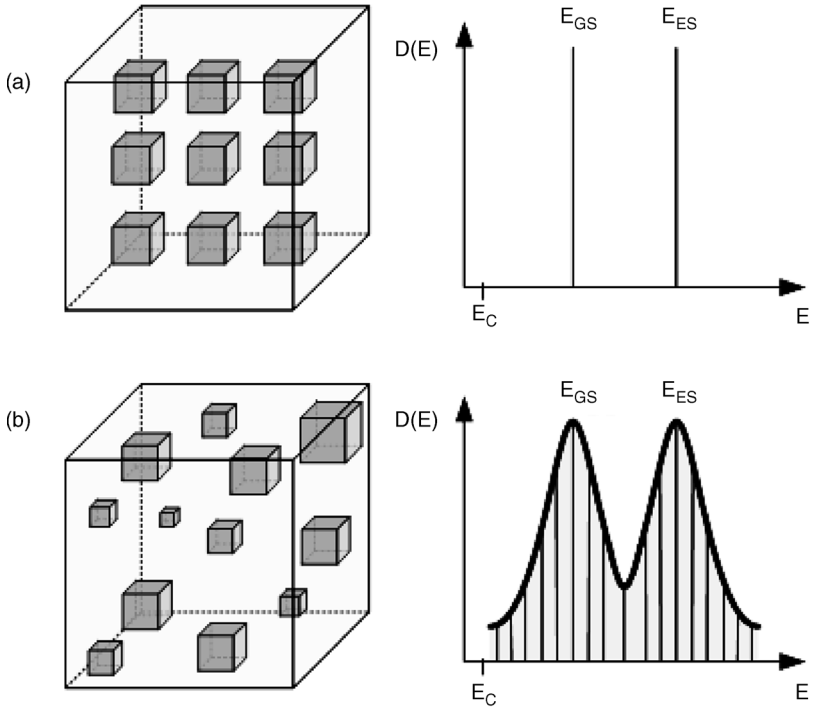

Figure 1.4 (*Right*) Schematic morphology and (*left*) density of states for charge carriers in (a) an ideal quantum dot system and (b) a real quantum dot system, where inhomogeneous broadening is illustrated.

elastic strain in different parts of the wafer will affect the level of energy [30]. The effects of inhomogeneous broadening on the density of states are schematically illustrated in Figure 1.4. The recent results from a number of research groups, including our own, indicate that because of this specific characteristic these structures could be designed to offer some advantages in ultrafast science and technology. This is because a very wide bandwidth is available for the generation, propagation, and amplification of ultrashort pulses, which can be tuned across a broad spectral latitude. Moreover, well-established growth technologies for such structures allow this broadening to be controlled and tailored by selecting QD layers with suitable size distributions [31, 32]. However, to date, only a small fraction of these possibilities have been realized, and optical pulses generated by quantum dot sources are one to two orders of magnitude longer than the inverse width of the inhomogeneously broadened gain spectrum. It is also important to stress that a highly inhomogeneously broadened gain also encompasses a number of disadvantages because it partially defeats the purpose of a reduced dimensionality, by broadening the density of states. Indeed, the fluctuation in the size of the QDs increases the transparency current and reduces the modal and differential gain [33, 34].

As for epitaxially grown QD layers, it has been shown that the variation in the dot size in QD-doped glasses leads to a change in the spectral location of the first excitonic absorption peak, giving a possibility of continuous absorption tuning to a substantial spectral extent [35].

1.3.2 Ultrafast Carrier Dynamics

In the initial studies of QD-based materials, it was thought that their charge carrier dynamics would be significantly slower than those of quantum well materials due to a phonon bottleneck effect [36, 37]. This effect was predicted on the basis that due to the discrete energy levels, electrons would not be able to relax via phonon interaction because it would not be possible to match the phonon energy; this expected limitation became known as *the phonon bottleneck*. Interestingly, experiments have demonstrated quite the opposite. As a consequence of access to a number of recombination paths for the carriers, QD structures exhibit ultrafast recovery times, under both absorption and gain conditions [38].

In several such assessments, the absorber dynamics of surface and waveguided QD structures were investigated by using a pump–probe technique (see, for example, Refs [39, 40]). This evaluation showed the existence of at least two distinct time constants for the recovery of the absorption. A fast recovery of around 1 ps is followed by a slower recovery process that extends to 100 ps (Figure 1.5). The fast recovery time is particularly useful for enabling saturable absorbers to mode lock lasers at high

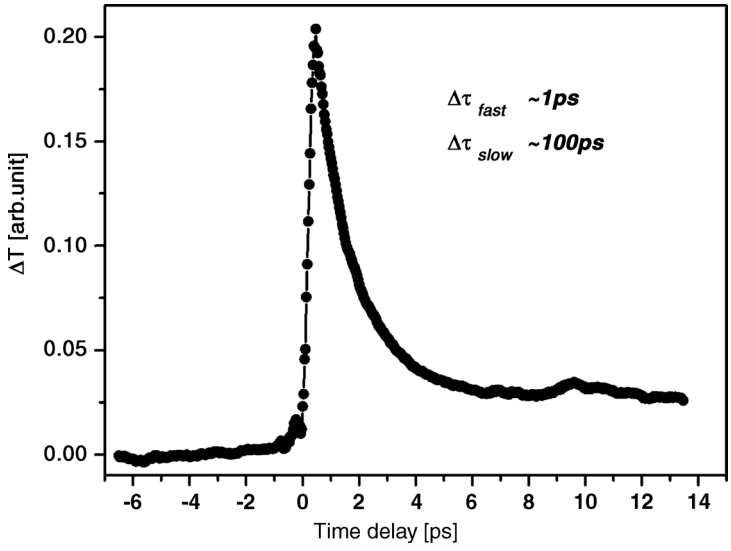

Figure 1.5 Pump–probe measurements of the carrier lifetime of a quantum dot waveguide device. $\Delta\tau_{fast}$ and $\Delta\tau_{slow}$ are fast and slow recovery times, respectively, and ΔT corresponds to the temporal changes in transmission.

repetition rates, where the absorption recovery should occur within the round-trip period of the cavity.

QDs suspended in glasses also exhibit fast carrier dynamics. Phonon bottleneck (see Section 2.3) has not been observed in these materials because of the existence of other relaxation channels for the carriers. These channels can be surface/defect states, electron–hole interaction in some materials [41], or multiphonon emission [42]. Their bleaching relaxation kinetics also exhibits a biexponential character, with fast and slow components, where the fast component decreases with reduction in the QD radius [35]. A review of all these dynamic processes can be found in Ref. [43].