4 Epitaxial Growth and Electronic Structure of Self-assembled Quantum Dots

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Semiconductor quantum dots have proved to be a convenient tool for exploring the physics of carriers and excitons confinement in zero dimensional structures. The rapid progress in lithography techniques as well as self-assembling crystal growth techniques have also been responsible for advances in this field and the growing variety of quantum dot devices that are under investigation. In this first lecture, I will review the fundamentals thermodynamics and kinetics processes involved in the self-assembled quantum dot formation on both planar and patterned substrates. The zero dimensional characteristics of the QDs will be addressed along with results showing the importance of on many body effects in single and coupled QDs.

INTRODUCTION

The use of strain induced islands as a process for forming self assembled quantum dots (QDs) (Leonard, 1993; Marzin, 1994; Xie, 1995) in III-V semiconductors using epitaxial methods has been part of a large effort to exploit the novel quantum properties which arise from the 3 dimensional quantum confinement of carriers. Using the growth of self assembled islands via a coherently strained epitaxial layer is more than a decade old and has proved an easy avenue for investigating and exploiting the physics of 3 dimensional (3D) carrier confinement in QDs.

The role of self assembled islands as a strain relieving process was first recognized in the investigation of SiGe/Si strained layers (Eaglesham, 1990). When an epitaxial film is deposited on a lattice mismatched substrate, under specific growth conditions and if the lattice mismatch is not too large (less than 10%), the elastic strain energy in the film builds up as the square of the lattice strain. The total energy in the film (including strain energy, interfacial energy and surface energy) is then minimized through the formation of coherently strained islands during growth.

The direct crystal growth of self-assembling QDs has been widely recognized as the easiest approach for forming self assembled QDs in a wide variety of strained semiconductor systems. Semiconductor self assembled QDs in the III-V compounds systems as well as II-VI and group IV heterostructures systems

(Leonard, 1993; Marzin, 1994; Xie, 1995; Petroff, 2001; Bimberg, 1998). The use of self-assembled QDs structures for investigating the physics of 3 dimensionally (3D) confined carriers has been extensive and provided a very convenient "laboratory bench" for studies of many body effects in semiconductors.

In this paper we will develop the newer methods for producing self-ordered QDs lattices. The well known electronic shell structure which we know for the atom also holds for the self assembled QDs. We will briefly review some of these properties and discuss some of the many body effects which dominate the quantum dot electronic properties as a consequence of the quantum confinement.

1) Formation of quantum dots, quantum rings and strain effects on island nucleation:

Thermodynamics and kinetics are both involved in the formation of self-assembled quantum dots. As illustrated in Figure 1 for the case of III-V compounds semiconductors, atoms falling on a clean substrate held at high temperature, will self assemble into smooth epitaxial atomic layers if the lattice mismatch between the material deposited and the substrate is not too large. The diffusion length of some of the group III elements deposited by molecular beam epitaxy (MBE) are sufficiently large to insure the layer by layer growth until a build up in the strain and surface energy of the epitaxial film switches the growth to the island mode. This change in the surface morphology is dictated by the minimization of the film energy. This interplay between the strain and surface energy of the film can be used, as we will see later to control the island nucleation and promote self-ordering of islands.

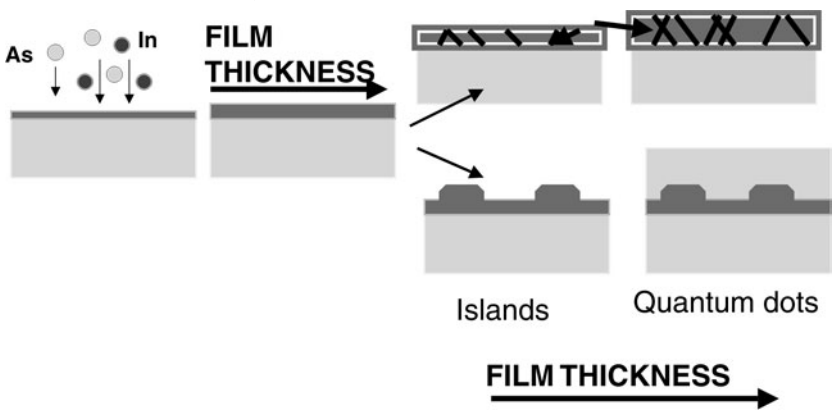

Figure 1 Schematic of the island growth process illustrated for the deposition of InAs on GaAs. Capping of the islands will transform them into quantum dots. An increase in the film thickness beyond the island formation stage will produce island coarsening and the introduction of dislocations.

As shown schematically in Figure 1, increasing the film thickness beyond the island formation stage will introduce dislocations. The growth of self-assembled quantum dots (QDs) is achieved by covering the smaller band gap material of the

islands with a wider band gap epitaxial film. This island growth process has been observed for wide variety semiconductor systems and has been used to produce self-assembled quantum dots. The general characteristics of the islands or quantum dots produced by self-assembling growth are:

a) A poor control over the size distribution of the islands. The size dispersion is in general >10%. Random island nucleation and coarsening are responsible for the wide size distribution.

b) A poorly defined shape and dimension for the islands. Once covered, the island shape changes through exchange reactions and diffusion processes. In many instances the shape of the island is not a hemispherical cap and is anisotropic,

c) A poorly defined composition of the QDs. Exchange reactions and diffusion processes will change the composition from the one programmed by the crystal grower.

d) A random distribution of the islands on the surface. Although the initial nucleation of islands takes place preferentially at step edges, random nucleation events on terraces will eventually dominate.

Several of these characteristics can adversely affect the performance of quantum dot devices made using the direct growth technique and a great deal of efforts has been directed to address some of these problems.

A possible approach to control the size and ordering of the islands is that of strain-controlled nucleation. The method makes use of the nucleation of islands on surface sites where a build up of strain has been introduced. Indeed by controlling the island nucleation process to well defined areas, it is possible to minimize random nucleation and promote a better island size uniformity (Tue, 1996). The interaction strain fields between islands can insure an identical growth

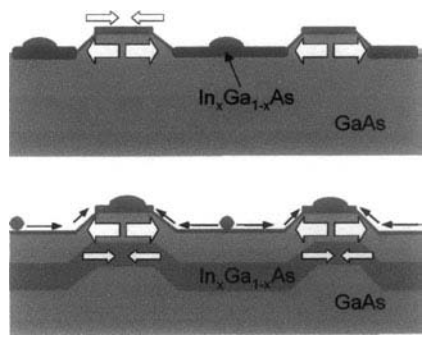

Figure 2 Schematics of two possible configurations for island growth on a patterned substrate. In the top, the strain distribution in the structure is illustrated by arrows and the crystal growth will preferentially occur in the valleys. In the bottom schematic, a coherently strained InGaAs stressor layer is used to enhance the strain on the mesa edge tops. The growth of islands will preferentially occur on the mesa tops where the strain build up is the largest.

rate for all islands. This method was initially introduced to order islands on a mesa ridge where the diffusion kinetics favored a build up strain on one edge of the mesa (Mui, 1995). Strings of InAs islands were produced in a patterned GaAs surface suing this method; Monte Carlo simulations (Tue, 1996) did show that enhanced island interactions would induce a significant narrowing of the islands size distribution.

The schematics in Figure 2 illustrate two extremes of the growth on a patterned substrate.

The thermodynamic suggest that if diffusion processes are fast enough, the InAs film will preferentially grow in the valleys present on the GaAs surface. As a strain relieving process, the InAs islands will therefore preferentially nucleate in the valleys on the GaAs surface. On the other hand, the thermodynamics and diffusion kinetics can be changed by introducing a local strain field on the surface. As shown in Figure 2 this is done by growing a coherently strained layer of InGaAs below the surface. In this case, the InAs film will grow more rapidly on the mesa tops and induce a preferential growth on InAs islands on top of the subsurface stressors (Lee, 2000).

2) Island and quantum dot lattices:

A patterned substrate composed of an ordered lattice of mesas is fabricated using an optical holographic process on a GaAs surface. The InGaAs islands are deposited by molecular beam epitaxy (Lee, 2000). As shown in Figure 3, the

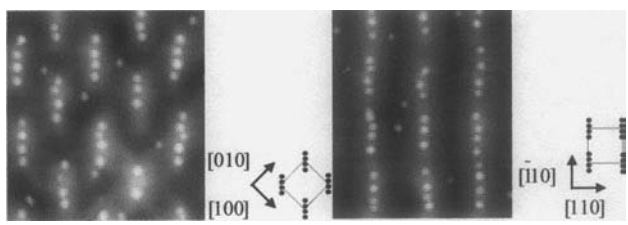

Figure 3 Examples of ordered InAs island lattices [7]. The InAs islands are deposited on a GaAs patterned substrate and the schematic of the unit cell of these two lattices correspond to each of the atomic force micrographs. The lattice parameter is 200 nm.

lattice orientation can be adjusted by the orientation of the mesa lattice on the prepatterned substrate. The two types of mesa lattices promote the formation of InAs islands on the mesa tops. The number of island in the lattice basis was found to depend on the mesa shape and width and on the In flux.

Figure 4 shows an example of an InAs islands lattice with a basis of one, two or three islands. A finite element calculations of the strain distribution in these structures indicates that the InAs islands nucleate at the surface sites where the stress is highest i.e. the mesa edges and end points of the mesa ridges. This effect is supported by our experimental results (Figure 4). The number of islands per

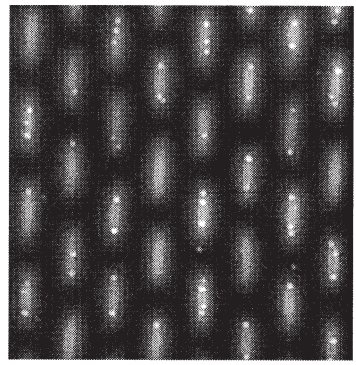

Figure 4 Atomic force micrograph of a lattice of mesas on which InAs islands were deposited using the strain engineered nucleation method. Note that the number of islands per mesa will vary between one and three. The islands nucleate preferentially on the surface sites where the strain is maximum. The lattice parameter for this example is 410 nm.

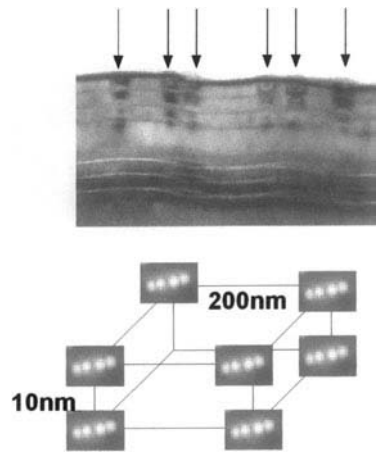

Figure 5 Cross section TEM through a 3-dimensional quantum dot lattice. The InAs stacked quantum dots along the <100>-growth direction are separated by a 10 nm thick GaAs layer. The quantum dots are detected through their associated strain fields. The bottom schematic is an idealized reconstruction of the three-dimensional quantum dot lattice with the dimensions of the unit cell indicated.

mesa point will therefore be greatly dependent on the shape of the mesas and on the In flux.

Using this method a good control over the mesa shapes should promote the formation of a narrower size distribution for the islands. Another benefit is to reach the highest possible island density locally since their density is limited by

the interaction stress fields between islands. Under optimal conditions and for a pyramidal shape mesa, one should be able to form lattices with one island per mesa.

Once a 2-dimensional island lattice is formed on the surface, it is easy to grow a 3-dimensional island lattice using the strain coupling between island layers. As shown in Figure 5, the 2 dimensional lattices of islands is replicated along the growth direction through the preferential nucleation of islands on top of each other along the growth direction if the interlayer spacing is smaller than ≈10 nm.

The future challenge will be to reduce the size of the unit cell by developing a patterning process which is cheap and suitable for a rapid processing of large areas.

The nucleation site engineering method may be a useful avenue for increasing the QDs density and this may lead to large improvement in the gain characteristics of QDs lasers (Bimberg, 1998).

QUANTUM DOT ELECTRONIC PROPERTIES

1) An "atom like" shell model for quantum dots:

One of the remarkable properties of the semiconductor QDs fabricated by epitaxial methods is their atom like electronic properties which come from the

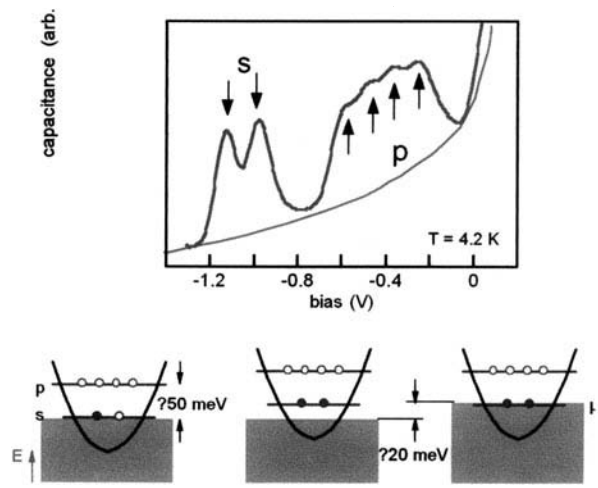

Figure 6 Capacitance voltage spectra of an InAs QDs ensemble showing the loading of the s (peaks at –1.18V and at –0.9V) and p shell electrons (peaks at positive voltages). The electronic levels for the s and p shell loading are indicated schematically along with the deduced values of the energy level differences [3].

3 dimensional carrier confinement inside the QDs. Over the last few years, the introduction of single QD photoluminescence spectroscopy (PL) have permitted a better understanding of many body effects which are present when more than one carrier or one exciton are confined to the QDs (Petroff, 2001). Measurement of QDs ensembles through a variety of techniques have also allowed to obtain a better understanding of the electronic level structure of these QDs.

The shell structure has been observed through capacitance (C-V) and infrared spectroscopy measurements on large ensemble of QDs (Drexler, 1999). Figure 6 shows the capacitance spectrum along with the relatively sharp peak structure associated with the s and p shell electrons. The Coulomb charging energy corresponding to loading of the second s electrons is measured to be ≈25 meV, The four peaks corresponding to the p shell loading reflect the cylindrical symmetry of the QDs potential which is found from measurements to be roughly parabolic. A similar picture emerges for the hole shell structure however the energy level differences for s and p shell holes are smaller (10 meV) than for electrons (50 meV) (Medeiros, 1995).

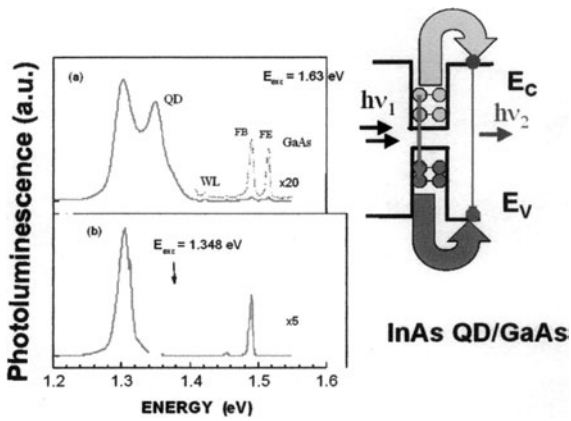

Figure 6 a) Photoluminescence spectra of a QDs ensemble. b) Excitation spectrum of a QD ensemble for an excitation energy of 1.348 eV. The schematic indicates a possible upconversion path corresponding to a two-step photon absorption process.

2) Many body effects in quantum dots:

Many body effects in quantum dots are observed most easily using photoluminescence spectroscopy. They are a direct consequence of the atomic shell structure and quantum confinement. They have been observed through the observation of multi-excitons and charged excitons in photoluminescence experiments (Drexler, 1999; Medeiros, 1995; Paskov, 2000; Dekel, 2001; Dekel, 2000). The very efficient upconversion process in highly excited quantum dots is also a manifestation of many body effects. We review briefly some of these experimental results.

a) Upconversion processes in quantum dots:

They are a consequence of the increased carrier interactions in QDs and of the shell filling effects.

As Figure 6 indicates, upconversion of electrons and holes injected with below band gap photons (E exc. = 1.348 eV) will generate higher energy excitons and emission of a GaAs (D^0X) at 1.428 eV. The pump power dependence of this upconversion process supports a two-step photon absorption process which could be favored by the strong carrier localization in the quantum dots (Paskov, 2000).

b) Photoluminescence processes in quantum dots:

Photoluminescence spectra of QDs ensembles as a function of increasing pump power reveal a complex emission line structure which is difficult to interpret because of size broadening effects and many body effects which can give rise to energetically closely spaced radiative recombination events. The most powerful approach to understand these multi excitonic recombination processes has been the single QD spectroscopy.

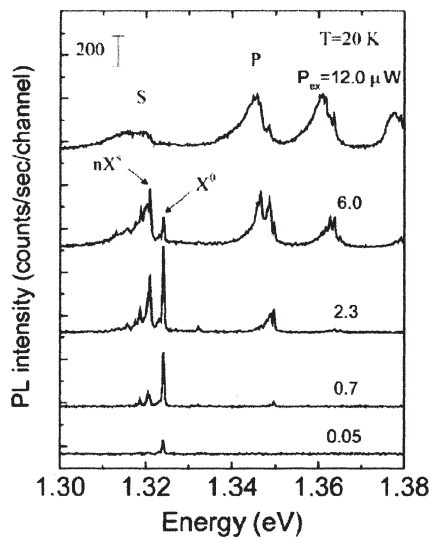

Figure 7 Micro-photoluminescence spectra of a single QD as a function of pump power. The radiative recombination of a single e-h pair gives rise to the X^0 emission line. For higher excitation powers, shell filling effects and Coulomb interaction between carriers give rise to a multiplicity of lines. The Coulomb interactions give rise also to the red shifted lines indicated by n X^s.

The blues shifted lines correspond to recombination originating from the p shell electrons and holes.

Photoluminescence spectra of single QDs give rise to extremely narrow emission lines (FWHM < 50 μeV). Recombination lifetime studies for closely spaced emission lines have enabled the interpretation of some of these

recombination processes and a better understanding of multi excitons in QDs. As shown in Figure 7, shell filling effects give rise to emission from the s and p shell electrons and holes. Coulomb exchange interactions give rise to a red shifted emission below the single exciton X^0 line. Identification of these red shifted lines is still controversial because of the presence of multiply charged excitons emission. However, the bi-exciton X^2 and X^- and $X^{-\ -}$ emission have been identified through an experimental studies (Dekel, 2001; Dekel, 2000; Warburton, 2000) and theoretical kinetics studies (Dekel, 2001; Dekel, 2000) of their recombination processes.

c) Excitons in coupled quantum dots:

The electronic coupling between two vertically stacked InAs quantum dots can be tuned by using an electric field (Shtrichan, 2002). This is achieved by incorporating them into an n-i-n structure. Using a micro-photoluminescence (micro-PL) setup to optically isolate a single quantum dot pair and measure the time-averaged photoluminescence as a function of applied voltage, we find that coupling between excited states of the two quantum dots leads to charge transfer from one QD to the other. The micro- PL spectra have been modeled by considering: a) a field dependent charge transfer with a phonon assisted tunneling and b) the many-body spectrum of a quantum dot molecule for different carrier configurations.

In the example shown in Figure 8 the two quantum dots are spaced by 45Å. The applied electric field is tuned to allow transfer of an electron of one QD "s" state to the adjacent QD "f" state. The good match between the experimental and computed spectra is consistent with the formation of several charged states of the excitons (Shtrichan, 2002).

The main peaks in the extreme voltages spectra (± 0.8 V) are related to several configurations of neutral excitons in QD1: $1X_S$ (1.2599 eV), $2X_S$ (1.2577 eV), $3X_S$ (1.2484 eV, 1.2582 eV), $3X_P$ (1.291 eV). The spectrum at 0 V is dominated by configurations of negatively charged excitons: $1X_S^-$ (1.2574 eV),

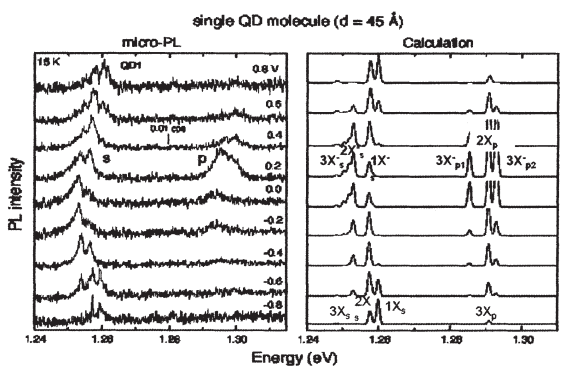

Figure 8 Measured and calculated micro-PL spectra of 45 Å coupled QD molecule at different external applied voltages. The computed spectra include a broadening parameter of 0.5 meV. The various charged states of the excitons are also indicated.

$2X_S^-$ (1.2529 eV), $2X_P^-$ (1.2907 eV), $3X_S^-$ (1.2483 eV, 1.2503 eV, 1.2517 eV), $3X_P^-$ (1.2853 eV, 1.2928 eV). The calculated spectra reproduce well the main features of the experimental spectra. A similar calculation, which does not take into account charge transfer between the dots, leads to a qualitatively different spectral behavior. Thus, the theoretical model supports our main conclusion: in this QD molecule device, charging of one QD from the other can be tuned by an external electric field.

CONCLUSIONS

A better control of the QDs growth and ordering processes are emerging. Still much remains to be done to understand and improve size distribution, shape and composition of the epitaxial QDs. The finding that QDs are behaving as atoms from an electronic point of view is certainly attractive and will lead to several new types of devices. The understanding of many body effects in QDs has progressed rapidly however in most cases this has been done for QDs loaded with electrons and holes. There is a need to carry out single QD spectroscopy with QDs loaded with only one type of carriers to better our understanding of Coulomb and Auger processes in QDs.

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