

1995

Luminescence from Semiconductor Quantum Wires, Quantum Dots, and Monolayer Quantum Wells: Bottleneck and Localization Issues

C. M. Sotomayor Torres
University of Glasgow, clivia@uni-wuppertal.de

P. D. Wang
University of Glasgow

N. N. Ledentsov
A. F. Ioffe Physico-Technical Institute

Y. -S. Tang
University of Glasgow

H. Qiang
University of New York
Follow this and additional works at: <https://digitalcommons.usu.edu/microscopy>

 Part of the [Biology Commons](#)
See next page for additional authors

Recommended Citation

Sotomayor Torres, C. M.; Wang, P. D.; Ledentsov, N. N.; Tang, Y. -S.; Qiang, H.; Pollak, F. H.; Ghaemi, H. F.; and Goldberg, B. B. (1995) "Luminescence from Semiconductor Quantum Wires, Quantum Dots, and Monolayer Quantum Wells: Bottleneck and Localization Issues," *Scanning Microscopy*. Vol. 1995 : No. 9 , Article 16.

Available at: <https://digitalcommons.usu.edu/microscopy/vol1995/iss9/16>

This Article is brought to you for free and open access by the Western Dairy Center at DigitalCommons@USU. It has been accepted for inclusion in Scanning Microscopy by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.

Luminescence from Semiconductor Quantum Wires, Quantum Dots, and Monolayer Quantum Wells: Bottleneck and Localization Issues

Authors

C. M. Sotomayor Torres, P. D. Wang, N. N. Ledentsov, Y. -S. Tang, H. Qiang, F. H. Pollak, H. F. Ghaemi, and B. B. Goldberg

LUMINESCENCE FROM SEMICONDUCTOR QUANTUM WIRES, QUANTUM DOTS AND MONOLAYER QUANTUM WELLS: BOTTLENECK AND LOCALIZATION ISSUES

C.M. Sotomayor Torres*, P.D. Wang, N.N. Ledentsov¹, Y.-S. Tang,
H. Qiang², F.H. Pollak², H.F. Ghaemi³ and B.B. Goldberg³

Nanoelectronics Res. Ctr., Dept. Electronics and Electrical Engg., Univ. Glasgow, Glasgow G12 8QQ, U.K.

¹Permanent address: A.F. Ioffe Physico-Technical Institute, 194021 St. Petersburg, Russia

²Physics Dept. Brooklyn College of the City University of New York, Brooklyn, NY 11210, USA

³Physics Department, University of Boston, 590 Commonwealth Avenue, Boston, MA 02215, USA

Abstract

Semiconductors nanostructures are fabricated using a range of techniques which inevitably have an impact in the resulting optical properties. Multilayers are grown by epitaxial techniques with a varying degree of uniformity in thickness, composition, etc., all leading to localisation effects in two-dimension. These multilayers are patterned to fabricate wires and dots using, in this case, electron beam lithography and dry etching. The fabrication steps contribute to modifications of the optical properties, beyond the expected purely confinement-related effects.

An overview of linear and modulation spectroscopy is presented to demonstrate the impact of fabrication steps as well as of lateral confinement upon the emission from wires and dots. We focus on photoreflectance of GaAs-GaAlAs dots and Si-SiGe wires as a probe of strain relaxation. Near-field scanning optical microscopy of single dots of GaAs-GaAlAs at helium temperatures illustrates the potentials of using scanning probe techniques to study the underlying quantum mechanics of nanostructures. Finally, we suggest that a combination of lateral exciton confinement and exciton localization is a possible way forward to realise high emission efficiency nanostructures.

Key Words: Quantum wires and dots, excitons, electron-phonon interaction, localization, energy and momentum relaxation, InAs-GaAs quantum wells, luminescence, luminescence excitation, photoreflectance, near-field scanning optical microscopy.

*Address for correspondence and current address:

Clivia M. Sotomayor Torres
Institute for Materials Sciences and
Department of Electrical Engineering,
University of Wuppertal, Gauss-str.20,
42097 Wuppertal, Germany

Telephone number: 49-202-439-2920

FAX number: 49-202-439-3037

E-mail: clivia@uni-wuppertal.de

Introduction

The purpose of this contribution is to provide an overview of progress in the understanding of excitons in semiconductor quantum dots and wires vis-a-vis highly localised excitons in submonolayer quantum wells of InAs-GaAs from the point of view of efficient exciton radiative recombination.

Semiconductor quantum wires and dots are unique condensed matter systems where electron and hole localisation can be achieved by lateral confinement down to quasi zero-dimensions. These nanostructures are realised by a variety of techniques including electron beam lithography and dry etching. Fluctuations in the 2-D quantum well thickness of the starting material and in the alloy composition of one or two of the materials involved are generally compounded with fabrication-related effects to produce optical signals testifying to confinement mixed with strain changes, localisation and the presence of non-radiative centres.

When considering light emission, the main quasi-particle studied is the exciton. In semiconductors, the spatial extent of the exciton is a length scale to determine whether the system under study is under separate confinement or under exciton centre-of-mass confinement (Kash, 1990). In the case of most GaAs-based structures, the size is in the range of approximately 30 to 150 nm. This lateral confinement results in a strongly modified density of states (DOS): from the two-dimensional (2-D) case featuring a step-like function, through the one-dimensional (1-D) case with a DOS exhibiting a sharp increase with a tail dropping as $E^{1/2}$ to higher energies, to the zero-dimensional (0-D) case where the DOS becomes a series of δ -functions (Weisbuch and Vinter, 1991; Stern, 1992). One driving force was based on the possibility of obtaining a giant oscillator strength which could lead to lasers, with minimum threshold current density, and strong optical non-linear devices among a range of devices.

Luminescence spectroscopy has been a major experimental tool to assess the emission strength of nanostructures. In general it was found that as the lateral size

decreased so did the luminescence intensity (see, for example, Forchel *et al.*, 1990; Sotomayor Torres *et al.*, 1990; and Clausen *et al.*, 1989). The search began for the reasons of this poor luminescence yield. Several factors were considered including damage to the side-walls, strain changes, poor control of the lateral size uniformity, among others. Several models have been put forward and below we describe one based only on intrinsic phenomena invoking inhibited energy and momentum relaxation (Benisty *et al.*, 1991). We evaluate it with respect to real nanostructures and to recent results. It emerges clearly that one need is for fast *in-situ* non-destructive characterization during fabrication and the other is the need to study optically single nanostructures to avoid the line-shape broadening resulting from probing many nanostructures with lateral size fluctuation ranging from 1 (best case) to 30% (worst case) of the mean size.

More recently new experimental results have become available concerning: (a) optical properties of modulation doped quantum dots and wires (see, for example, Goñi *et al.*, 1991 for wires; Wang *et al.*, 1994a for dots) with an insight into many-body interactions in 1- and 0-dimensions, accompanied by theoretical developments (Gumbs *et al.*, 1994); and (b) structural characterisation of dots and wires using reciprocal space maps obtained by triple-axis X-ray diffraction (Darhuber *et al.*, 1995). These two recent developments are beyond the scope of this article and will be discussed elsewhere.

Excitons in Deep Etched Nanostructures

The realisation of lateral potentials to form semiconductor nanostructures, such as quantum dots (QD) and quantum well wires (QWW) has been made possible by a variety of techniques including: (a) The use of surface stressor pioneered by the Bellcore group (for a review, see, Kash, 1990) and pursued in a slightly different form by the Santa Barbara group (Tan *et al.*, 1991) which resulted in confinement energies in the range of 12-16 meV; (b) Surface barrier modulation (Greus *et al.*, 1993) which uses a related concept, by modulating the top barrier of the quantum well, resulting in an enhancement of the energy in quantum well areas closer to the surface with a blue energy shift of around 7 meV for 20 nm wire wide.

There is a whole family of direct-growth techniques for wires and dots, including QWW in V-grooves (see, for example, Kapon *et al.*, 1993), and dots (Leonard *et al.*, 1993). Whereas the emission efficiency is high compared to etched dots and wires, there are some difficulties with these approaches. For example in QWW, there are exciton transport mechanisms which appear to limit the lower end of the laser threshold current and, concerning the dots, the size distribution is not easy to

control. Several groups are working in ways to improve the direct-grown of nanostructures (Arakawa, 1994).

Fabrication of deep etched nanostructures

Deep etched nanostructures are fabricated by combined electron beam lithography (EBL) or holography and dry or wet etching. The work in Glasgow uses EBL and dry etching in SiCl_4 for GaAs deep etched wires and dots (see, for example, Wang *et al.*, 1992a). A similar approach is used by several other groups. Figures 1 and 2 show an scanning electron micrograph of an array of GaAs-GaAlAs dots of 180 nm diameter and wires of 100 nm width, respectively. The main drawback is the presence of a semiconductor-air interface of these free-standing nanostructures, which limits the observation of optical processes to sizes down to 20-30 nm, due to both surface effects and the phonon "bottleneck" (Benisty *et al.*, 1991).

The luminescence spectrum of an array of 60 nm GaAs-Ga_{0.70}Al_{0.30}As QD is shown in Figure 3 where the upper spectrum corresponds to a control mesa and the lower spectrum corresponds to the dot array for which a magnification of x100 has been used to display them in the same scale. It is clear that the emission intensity decreases with negligible impact on line-width broadening. Luminescence excitation spectra of 60 nm wide QWW in two polarization and of the control mesa are shown in Figure 4 (left) clearly showing the heavy-hole and light-excitons and the 1-D confined heavy-hole exciton states. These energies are plotted as a function of wire width in Figure 4 (right) and agree fairly well with a simple confinement model using the envelope function approximation (P.D. Wang *et al.*, unpublished).

Luminescence limiting mechanisms in quantum dots and wires

As mentioned above, much effort has been invested to obtain evidence for enhanced oscillator strength by measuring the integrated emission intensity as a function of lateral size (width for wires and diameter for dots) normalising for the area covered after etching, with respect to the 2-D sample, with no success. Various models based on the effect of the surface upon radiative recombination were proposed (Forchel *et al.*, 1990; Clausen *et al.*, 1989), which suggested the existence of a "dead" layer, the thickness of which was fabrication process dependent. The models needed an estimate of the surface recombination velocity, assuming a given exciton diffusion length. The models assumed that excitons were photo-created in the quantum dot or wire and would diffuse to the nanostructure surface recombining there non-radiatively, hence for larger structures there would be a higher probability of observing emission from dot- and wire-like structures. The "dead" layer models suggested that the emission would be too weak

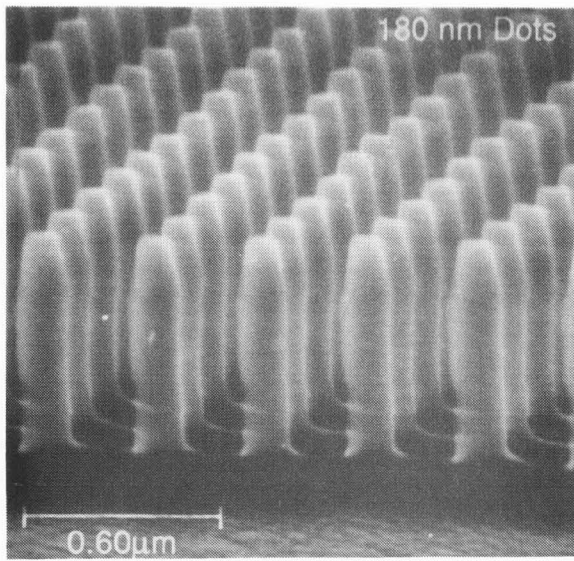


Figure 1. Scanning electron micrograph of an array of GaAs-GaAlAs 180 nm diameter dots.

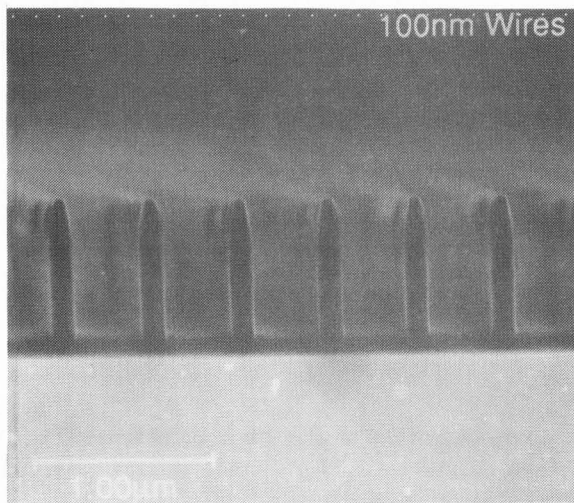


Figure 2. Scanning electron micrograph of an array of GaAs-GaAlAs 100 nm wide wires.

to allow observation of quantized energy levels in the smallest structures, as the surface-related non-radiative process would be dominant. Most experimental data supported this approach. Improvements on the emission intensity for a given lateral size were obtained by concentrating in materials of known lower surface recombination velocity, such as GaInAs-InP (Forchel *et al.*, 1990), which demonstrated that the surface played a significant role in deep etched structures.

A controversial model, based only on intrinsic

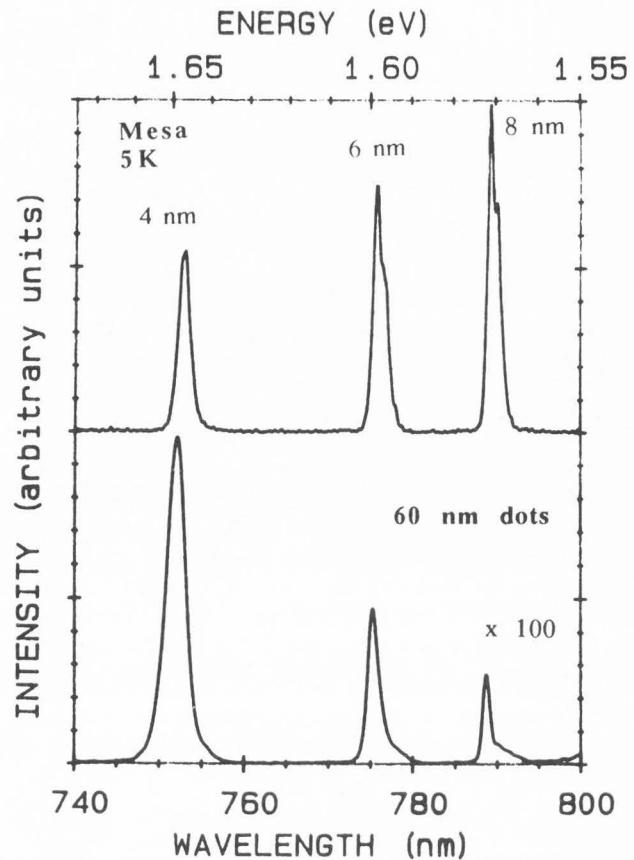


Figure 3. 5K luminescence spectra of GaAs-Ga_{0.70}Al_{0.30}As multiple quantum wells with well thicknesses of 4, 6 and 8 nm, (top) a control mesa and (bottom) 60 nm quantum dots.

mechanisms, was proposed to explain the decrease in luminescence intensity as a function of lateral size (Benisty *et al.*, 1991). It went like this: For GaAs-based nanostructures, the energy separation of the electronic levels for lateral sizes around 150 nm is of the order of a few meV, which is also valid for other comparable materials. This energy spacing is too small for the electron to interact with an optical phonon. Relaxation by acoustic phonons is already inhibited in wires and dots (Bockelmann and Bastard, 1990) due to the limited range of wave vectors available in 1-D and 0-D, compared to the 2-D case, thus, electrons tend to accumulate in higher-lying energy levels, a sort of "bottleneck", spending there times longer than the non-radiative recombination time. In other words: for radiative recombination to occur, both electron and hole have to be at the bottom of their respective bands with compatible quantum numbers. The slower energy and momentum relaxation increasingly prevents that from happening as the lateral dimensions become smaller. A comparison of this

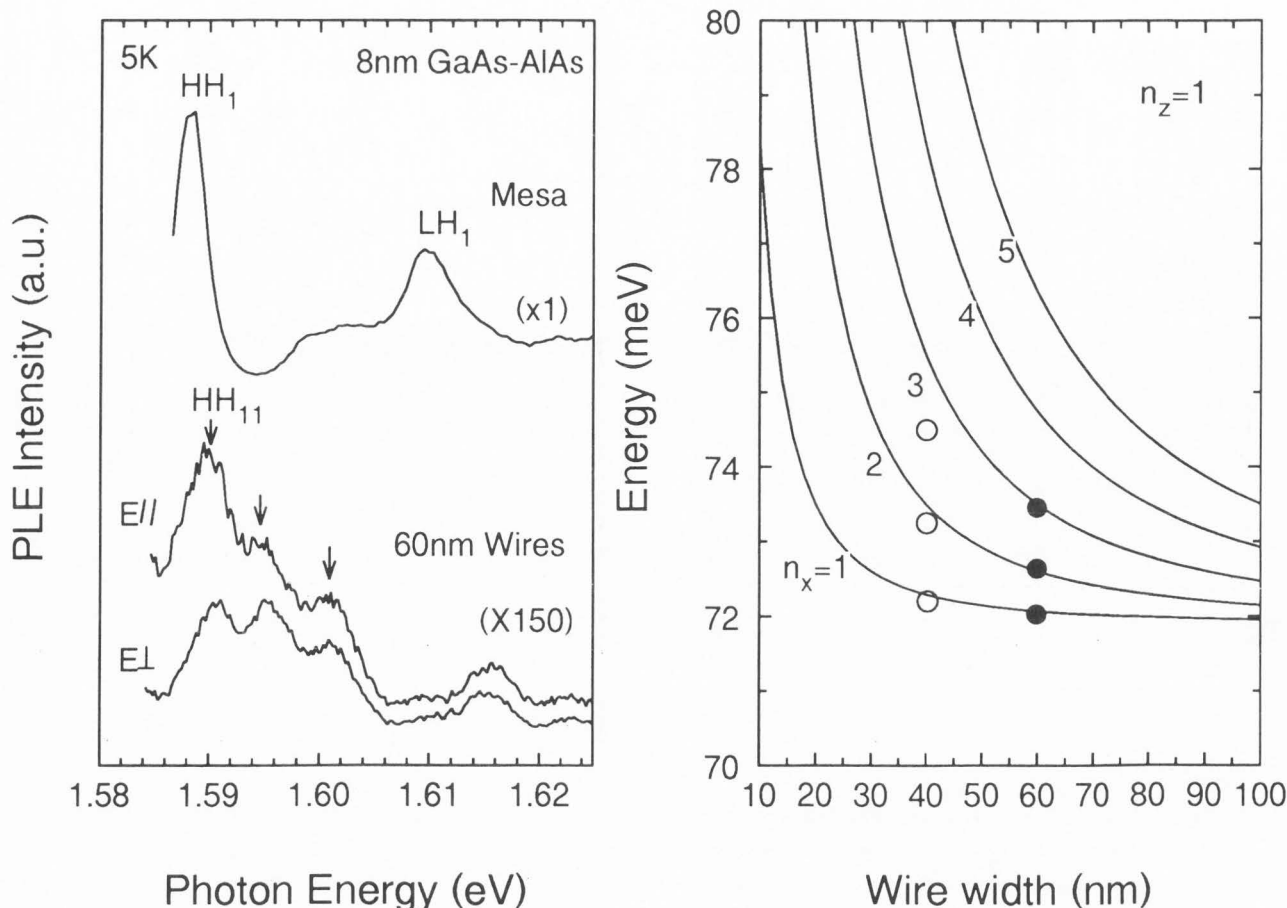


Figure 4. Left: 5K Luminescence excitation spectra of a multiple quantum wells of 20 x (8 nm GaAs and 10 nm AlAs barriers): the top spectrum corresponds to the control mesa and the middle to polarisation parallel to the main axis of the wires and the bottom one to perpendicular polarization. Right: The dependence of the heavy-hole exciton $n=1$ states confined to 1-dimension as a function of wire width.

model to experimental data, suggested that both, intrinsic (bottleneck) and extrinsic (dead layer) mechanisms controlled the emission strength (Wang *et al.*, 1992b). For larger structures, the "dead layer" approach gave a better fit to the data, whereas for smaller structure the "bottleneck" provided a cut-off size.

Moreover, Bockelmann (1992) calculated that for a given quantum dot size (e.g., a box of 100 x 100 nm x quantum well thickness, L_z), the acoustic phonon scattering time at 4K depended upon L_z , exhibiting a damped oscillatory behaviour peaking at around $L_z = 2.5$ nm and having a subsidiary maximum near 7 nm. We fabricated dots of various diameter in a series of GaAs-GaAlAs single quantum well samples with different L_z : 2.3, 4.5, 6.9 and 10.7 nm (Wang *et al.*, 1993a). The results are shown in Figure 5 demonstrating clearly that the integrated emission intensity at 4K, accounting for area coverage, was higher for all dot sizes fabricated in the sample with well width 2.3 nm and thus, confirming

the predominant role of acoustic phonon scattering.

The status of the bottleneck is as follows: (1). Direct evidence is not easy to obtain since it is virtually impossible to avoid the influence of extrinsic process ignored by the model; moreover, many experiments ignore the effect of carrier capture into the quantum well by performing luminescence experiments pumping optically above the barrier layer band gap. (2) Indirect evidence points to the validity of taking acoustic phonon scattering as the main energy relaxation mechanism. (3) If interband transitions are inhibited then there must be a higher probability for inter-subband transitions (in the infrared), but so far there are no studies carried out using simultaneous emission and infrared absorption/emission studies. (4) It is clear that the bottleneck model needs further development to include extrinsic (surfaces, impurities) phenomena, electron-electron (Auger scattering) and excitonic effects.

With respect to the last point, there have been at-

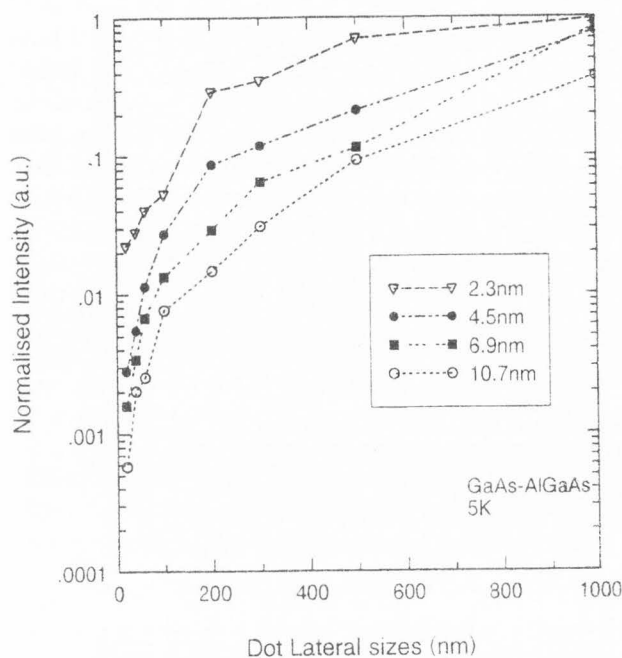


Figure 5. Normalized integrated luminescence intensity of quantum dots of GaAs-GaAlAs as a function of dot diameter for various quantum well thicknesses demonstrating the importance of acoustic phonon scattering.

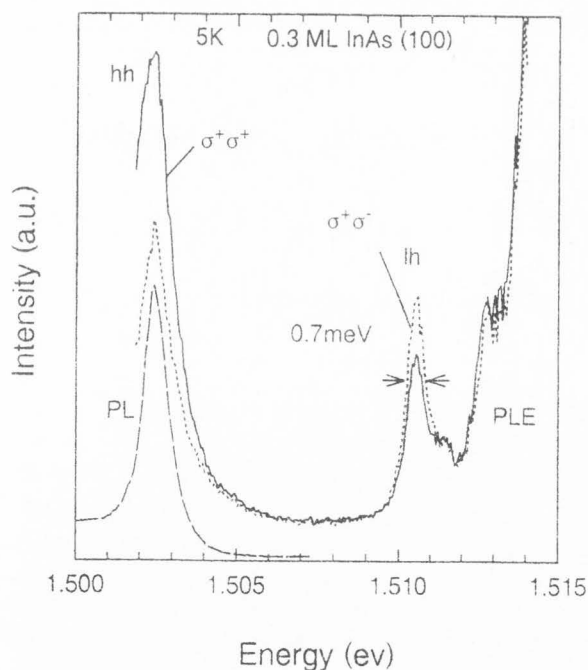


Figure 6. Photoluminescence (PL) and photoluminescence excitation (PLE) at 5K of (100) GaAs containing 1/3 InAs monolayer.

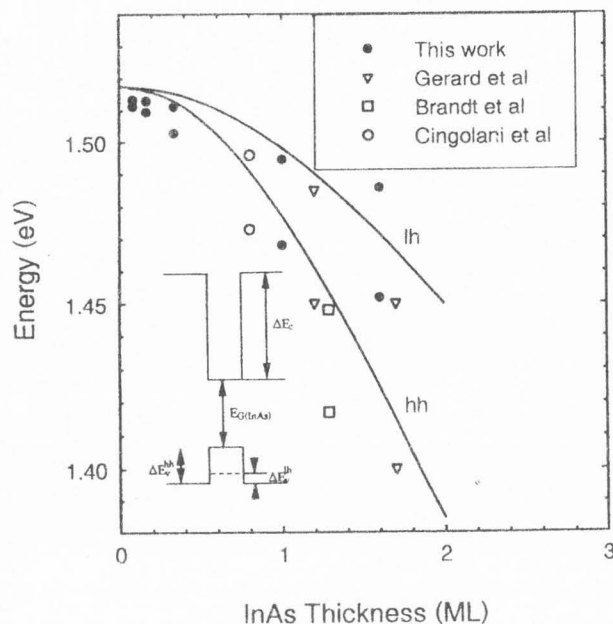


Figure 7. 4K Heavy-hole and light-hole exciton transitions in GaAs-InAs ultrathin quantum wells as a function of InAs monolayer thickness. The transition energies were measured by photoluminescence excitation. The inset is the band alignment diagram for InAs/GaAs heterostructures. The full circles are our work, the inverted triangles are from Gerard and Marzin (1988), the squares are from Brandt *et al.* (1990) and the circles from Cingolani *et al.* (1990). Solid lines in the figure are the effective mass calculations including strain-modifications of the band parameters at 4K: energy gaps of InAs, GaAs and InAs embedded in GaAs are taken as 0.418, 1.518 and 0.533 eV, respectively. For the 1 ML sample the conduction band, heavy hole valence and light-hole valence band offsets are taken as 0.689, 0.295 and 0.089 eV, respectively. All values were calculated assuming an InAs-GaAs lattice mismatch of 6.8% and conduction band non-parabolicity.

tempts to include second order multiphonon scattering (Inoshita and Sakaki, 1992) which would bring the scattering time closer to the radiative recombination time. The issue is then the probability of these processes. One way of enhancing multiphonon scattering is to design very carefully the nanostructures so that the difference between the confined energy levels is an integer multiple of say, LO phonons, as proposed by Arakawa (1994). Attempts to include many body interactions, such as, electron-electron correlation, did not enhance sufficiently the matrix element to overcome the bottleneck (Bryant, 1992). Auger processes have been proposed (Bockelmann and Egeler, 1992) and await experimental test.

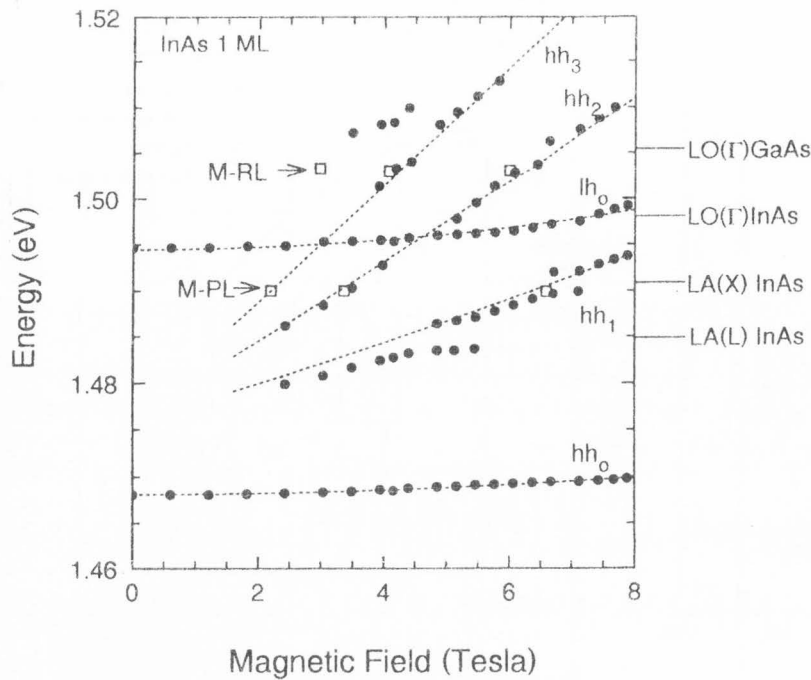


Figure 8. Transition energies from luminescence excitation as a function of magnetic field at 4K for 1 ML of InAs embedded in (100) GaAs. The dashed line is the theoretical fit based on an effective mass approach. Landau-level crossing and anti-crossing can be seen at energies matching those of the InAs zone boundary. Magneto-resonant luminescence (M-RL) data and magneto-luminescence (M-PL: obtained from luminescence intensity profiles as a function of magnetic field under resonant conditions) are both also shown in the figure.

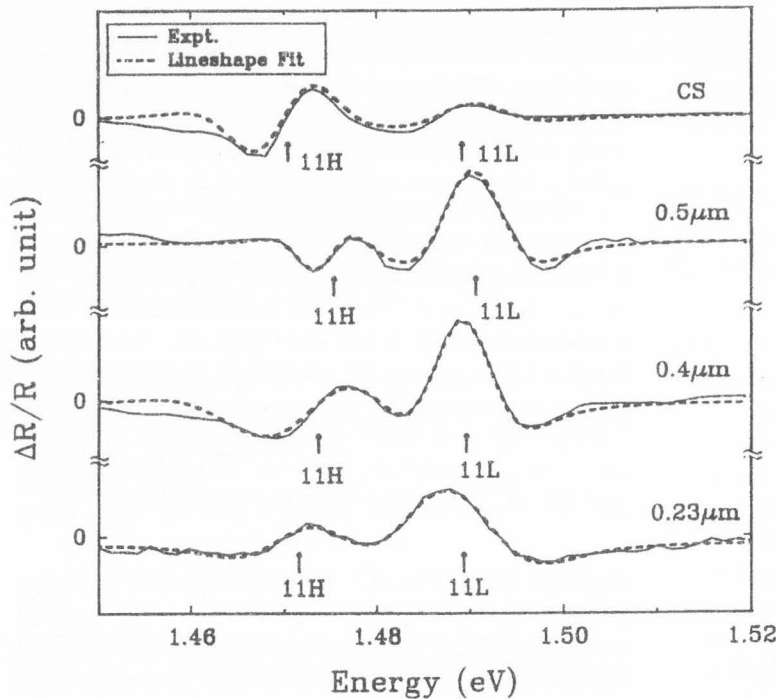


Figure 9. Room temperature photoreflectance (PR) spectrum ($\Delta R/R$) of the control sample, and of 0.5, 0.4 and 0.23 μm diameter GaAs-Ga_{0.7}Al_{0.3}As deep etched quantum dots.

Finally, recent developments including excited states of the exciton in a dot as levels participating in the relaxation has resulted in a higher probability of observing emission from the ground state in dots, since the conduction and valence band states are connected via components of the exciton wave-function built with electron and hole levels (Bockelmann *et al.*, 1994). These findings suggests that one direct way to minimize the bottle-

neck is to enhance the probability of transitions involving states with extended wave-vector k , such as, for example, iso-electronic impurities. Here, the quantum dot would ensure that other than surface effects the electron-hole pair would feel primarily the capture cross-section of the iso-electronic impurity and thus lead to a high quantum efficiency.

Exciton localisation in quantum wires

A quantum wire has one degree of freedom since carriers are free to move along the wire axis. Therefore, it is conceivable to think of excitons diffusing along the wire, if there were no traps, no relevant variations in the electrostatic potential and negligible surface roughness. When the normalized integrated luminescence efficiency was studied as a function of wire length for a given wire width, it was found that there were at least two regimes, depending on the quality of the starting material in terms of the probable concentration of localisation centres.

In high quality GaAs-GaAlAs quantum well samples, in terms of narrow line-widths and low impurity concentration, it was found that for 100 nm wire width, the normalised integrated emission intensity increased as the wire length decreased (Leitch *et al.*, 1992). This was explained by considering the concentration of background impurities, which for these sample series was in the region of low 10^{14} cm^{-3} , thus, a shorter wire will, on average, contain fewer impurities than a longer wire.

However, in a lattice matched GaInAs-InP 7 nm single quantum well, with a full-width at half maximum (FWHM) of 14 meV, the normalised integrated intensity of quantum wires was found to remain independent of wire length (MacLeod *et al.*, 1993). Clearly, the quantum well layer is a ternary alloy and as such it is likely to have alloy fluctuation potentials which compounded with quantum well thickness fluctuations tend to result in a system with many exciton localisation centres. This hypothesis was demonstrated by measuring the emission FWHM as a function of temperature. It was found that the FWHM has a minimum near 15K and then increased again. This is typical of systems with localisation centres which become ionised as the thermal energy enables excitons to escape and migrate in the crystal.

So what is the relevance to this work? It points out to the issue of exciton transport in quantum wires, both in the V-groove variety (see, for example, Kapon *et al.*, 1993) and in the deep etched and overgrown ones (H. Schweitzer, private communication). What happens is that excitons are formed everywhere in the semiconductor when electrons are injected or electron-hole pairs are photo-pumped with energy above the energy gap of the barrier material. Excitons then migrate to the regions of lower energies, for example the crescent in the V-groove or the buried wire in the overgrown structures. While they migrate they interact (scattering and/or localisation) with interface roughness, thickness fluctuations, impurities, etc., and thus, the conversion efficiency of the structure of power input to radiative recombination at the wire ground state energy is no better than the best 2-D quantum wire laser. Quantitative work in this area has

been carried out by the Stuttgart University team (H. Schweitzer, private communication).

Excitons Bound to a Planar Arrangement of Localisation Centres

A novel approach of confining excitons involves the growth of corrugated superlattices (see, for example, Nötzel *et al.*, 1993) and clusters (Alferov *et al.*, 1992) on high index planes of GaAs. In both cases, a strong emission line is observed, which persists up to 400K (Ploog *et al.*, 1992). The emission has been said to come from quantum wires, however, it may be appropriate to consider the emission as arising from strongly bound excitons to the wire-like and ordered cluster-like geometry of GaAs in the AlAs matrix (Alferov *et al.*, 1992). These ideas have been extended to the InAs-GaAs system.

The growth of highly-strained InAs-GaAs heterostructures on GaAs substrates with different orientation has also attracted much interest (see, for example, Brandt *et al.*, 1990; Marzin *et al.*, 1990; Braslavets *et al.*, 1991; Fahy *et al.*, 1993). In addition to a strong fundamental interest in growth-related phenomena (Sela *et al.*, 1991; Ilg *et al.*, 1993), these structures have numerous practical applications in opto- and micro-electronics (Dutta *et al.*, 1993). These systems have been also seen as possible candidates for the creation of quantum wires and dots (Yazawa *et al.*, 1991; Brandt *et al.*, 1991).

Here, we concentrate on submonolayer coverage of InAs embedded in a GaAs matrix grown on (100) GaAs (Ploog *et al.*, 1992; Wang *et al.*, 1994b), which can be considered as an ultrathin quantum well for one monolayer (ML) or more. In the case of fractional monolayers, the structure can be regarded as GaAs with a highly ordered planar distribution of quasi-iso-electronic centres. Recent epitaxial crystal growth studies (Ledentsov *et al.*, 1994) have confirmed the transformations experienced by the InAs surface on (100) GaAs as the InAs layer thickness increases and as a function of growth interruption time, concluding that while submonolayer coverage is stable, monolayers show a marked tendency towards transformation into different arrangements, such as, islands and clusters. Recent developments in this family of structures are discussed below.

InAs submonolayer quantum wells in (100) GaAs

A series of samples of GaAs containing a layer of InAs grown by solid source molecular beam epitaxy (MBE) were studied (Wang *et al.*, 1994b, 1994c). The InAs layer thickness varied from 1/12 ML to 1.6 ML. Several observations are noteworthy: (1) The emission intensity of these samples is stronger for thinner InAs

monolayers. (2) The emission of 1 ML of InAs grown on (100) GaAs is narrower than that of 1 ML of InAs grown on (311) GaAs. (3) There is no measurable Stoke shift between the 5K luminescence and luminescence excitation for InAs thinner than 1/3 ML (see Figure 6), but there is an increasing Stoke shift with increasing InAs layer thickness, which makes luminescence unsuitable to determine transition energies for thicker InAs layers. (4) From optical anisotropy data, it is deduced that InAs arranges itself as molecular chains along the (011) direction. (5) For 1.6 ML of InAs, the exciton binding energy is enhanced by over 300% compared to bulk GaAs suggesting strong heavy-hole exciton confinement, whereas, the light-hole excitons are weakly bound due to significant strain effects (see Figure 7). (6) From magneto-luminescence, it is found that interband magneto-polarons associated with zone-edge InAs phonons interact with the Landau levels in a complex anti-crossing behavior (see Figure 8), arising probably from the lattice mismatch strain-induced field. (7) Hole bands mass-reversal has been observed for the sample with 1/3 ML, as deduced from its diamagnetic shift, probably arising from a combination of strain and molecular chain-like structure for fractional monolayer InAs in GaAs.

From the above, we conclude that ultrathin and sub-monolayer InAs-GaAs quantum wells are samples with unique optical properties which are governed by localisation of 3-D excitons to an array of binding centres formed by the molecular chains of InAs. The details of the localisation and binding remains to be studied. One possibility is that InAs behaves as an iso-electronic impurity. This is unlikely to be the only factor. Clearly, there are strain fields involved which may also enhance exciton migration towards the InAs island and wire-like chain. Recent scanning transmission micrograph, obtained by the Santa Barbara group, showed the beginning of the wire-like structure in a (2x4) InAs surface on (100) GaAs (Leonard *et al.*, 1994). More recently, Grundmann *et al.* (1995) have observed bright cathodoluminescence from a single dot-like structure of InAs in a (100) GaAs matrix with a line-width of < 0.2 meV, again with negligible Stoke shift. It is clear that this form of self-organised growth presents a very promising path for obtaining strong and narrow emission lines, which, combined with an increase in the exciton binding energy are likely to be used in room temperature optoelectronic devices.

Non-Destructive Characterization of Nanostructures

Examples have been shown above on the use of photoluminescence and luminescence excitation to characterize semiconductor dots and wires. We have also

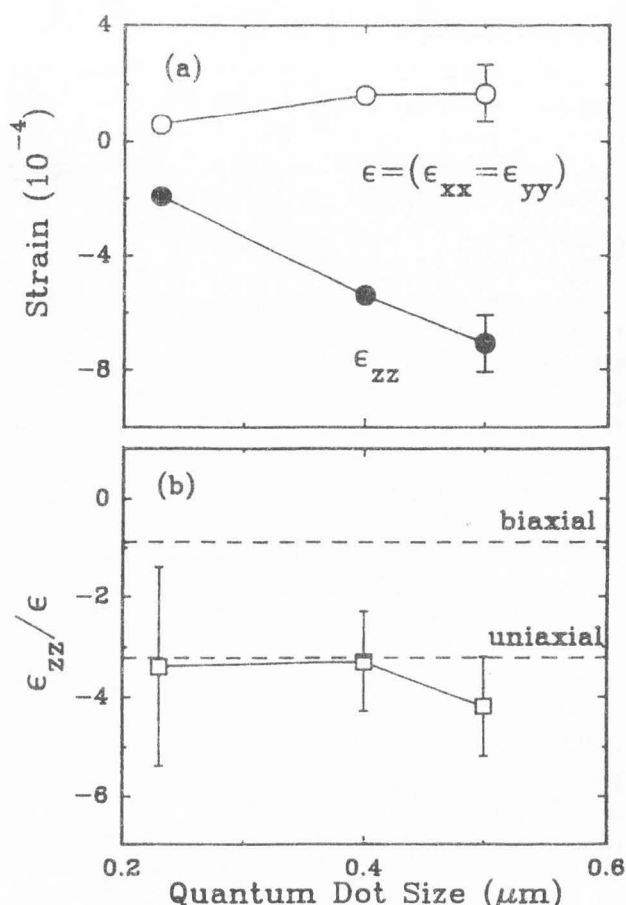


Figure 10. Resulting strain in dots as a function of dot diameter. It is shown to be uniaxial along the growth axis (b). The smaller the diameter the smaller the strain along the z-direction (a).

reported the use of micro-Raman spectroscopy for the study of GaAs-based nanostructures (Wang *et al.*, 1993b). In the course of our work, two techniques have proved to be immensely useful for the study of quantum dots. These are modulation spectroscopy, photoreflectance (PR) in particular, and near-field scanning optical microscopy (NSOM).

Photoreflectance

Studying the photoreflectance spectrum of deep etched GaAs-GaAlAs dots, it was found that the energy separation of the heavy- and light-hole exciton changed as a function of dot diameter. Moreover, the relative amplitude of the PR signal from the heavy- and light-hole excitons reversed with the light-hole one becoming stronger for dots compared to the control sample (Qiang *et al.*, 1994a, 1994b). Figure 9 shows the room temperature PR spectrum of the control sample, and of 0.5, 0.4

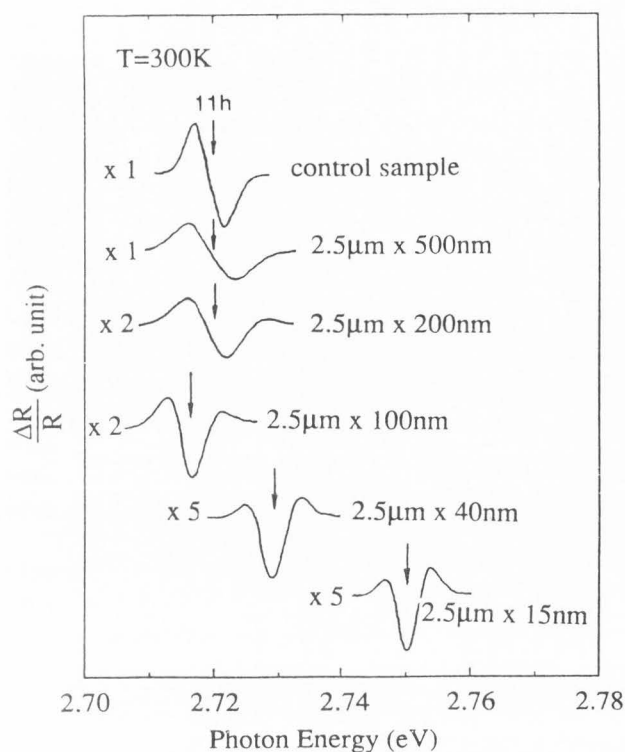


Figure 11. Photoreflectance of deep etched Si-Si_{0.8}Ge_{0.2} quantum wires at room temperature (see text for details).

and 0.23 μm diameter GaAs-GaAlAs deep etched quantum dots. Careful line-shape fitting allows the transition energies to be obtained in order to obtain the strain in the dots. It is assumed the strain is symmetric in the x-y plane which leads to direct relations to obtain the strain components from the energy shifts experienced by the heavy- and light-hole excitons neglecting non-linear terms. The hydrostatic and shear components are resolved and these are plotted in Figure 10 to show that the resulting strain in the dots is uniaxial along the growth axis (bottom diagram). Moreover, the smaller the diameter, the smaller the strain (upper diagram), suggesting that strain is relieved as the nanostructures become smaller. The lattice mismatch as well as fabrication-induced damage are likely to be responsible for the type of strain observed. More recently, high resolution triple axis X-ray diffraction has confirmed these findings (Darhuber *et al.*, 1995).

A similar situation is observed in Si-SiGe quantum wires. Tang *et al.* (1992, 1993a, 1993b) studied quantum wires down to 15 nm width fabricated in a 2-D hole-gas sample. The room temperature photoreflectance data of Figure 11 shows clearly that the direct gap minima of Si-SiGe moves first to lower energies show-

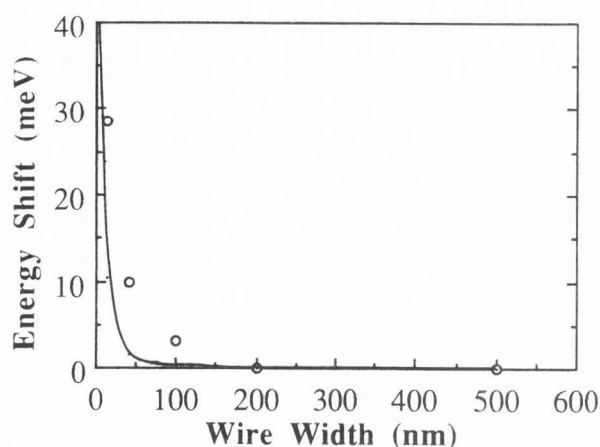


Figure 12. The energy shift of the no-phonon exciton luminescence of the SiGe quantum wire as a function of wire width (see text for details).

GaAs Quantum Dots

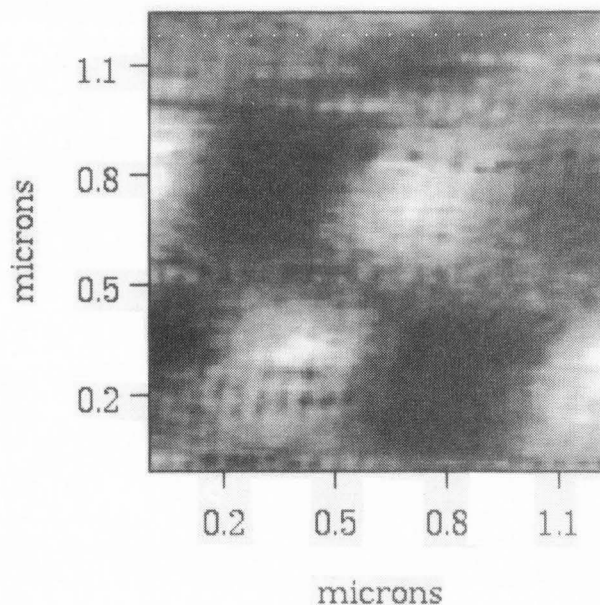


Figure 13. Optical reflectivity scan of etched 270 nm diameter GaAs-GaAlAs quantum dots obtained at 4K.

ing the effect of strain relief and then, for narrower wire width, the confinement wins over and a shift to higher energies is observed. Likewise, the photoluminescence peak associated with the no-phonon exciton of the SiGe quantum well is seen to shift to higher energies as shown in Figure 12. The solid line is a calculation where it has been assumed that the conduction band discontinuity is zero and it includes strain relief.

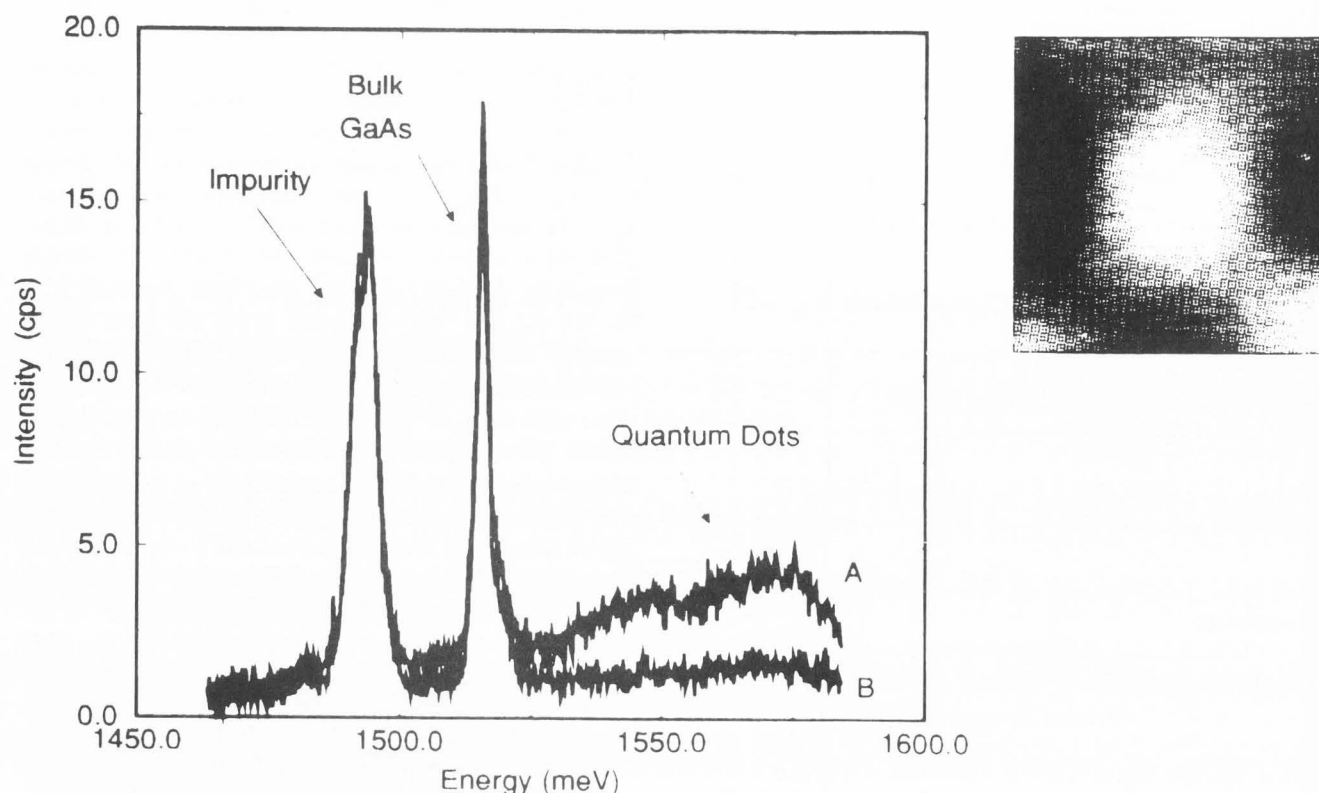


Figure 14. Right: Optical reflectivity image of a single quantum dot at 4K. Left: Luminescence emission spectrum at 4K recorded on the dot (spectrum A) and off the dot (spectrum B). See text for details.

The implications of these results concern both, the strain state of the starting material for quantum dot fabrication and the damage type and damage extent of the dry etching process. Using PR, it is expected that process optimization can be methodologically undertaken.

Near-field scanning optical microscopy

The power of NSOM is that it can resolve an electromagnetic wave with a spatial resolution in the $\lambda/40$ region (Betzig *et al.*, 1991). This brings unsurpassed spatial resolution, however the technique to obtain an emission spectrum from single dots at 4K is far from being a routine one. A collaboration with Boston University (Ghaemi *et al.*, 1995) has allowed us to obtain first images of GaAs quantum dots at 4K in reflection mode. Figure 13 shows the image of various 270 nm dots at 4K. Figure 14 (inset) shows the image of a single dot fabricated in a modulation doped multiple quantum well, while Figure 14 shows the single quantum dot luminescence spectrum recorded on the dot (spectrum A) and off the dot (spectrum B). A strong impurity line is observed at 1.490 eV and the bulk GaAs exciton is seen at 1.515 eV. The broad emission centred at 1.557 eV arises from the doped dot and is very similar to the far field spectrum from many dots. The broad line is asso-

ciated with the doping, with the multiple quantum well structure which may have quantum well thickness variations from quantum well to quantum well and with the slightly non-vertical etching. Clearly, there is a lot of progress to be made and these encouraging observations open the way to study single dot optical properties separating them from those of the ensemble. In a single dot, there is the potential of mapping the wave-function in the dot by monitoring the optical matrix element across the diameter. The possibility is also there for experiments in a magnetic field and for other forms of optical spectroscopy to be performed in single nanostructures. Further experiments are in progress.

Conclusions

It has been demonstrated that the optical properties of excitons in deep etched quantum dots and wires are strongly affected by energy and momentum relaxation as well as by localisation effects. The system formed by monolayer quantum wells of InAs-GaAs, with a highly ordered arrangement of exciton binding centres, proves to be an excellent test bed for exciton localisation and a most promising system for opto-electronic devices. It suggests that to realise the enhanced oscillator strength

originally expected of quantum dots, a combination of exciton confinement and localisation may be needed. The issue of electron-phonon interaction in quantum wires and dots still needs attention as the final work remains to be done. Information on exciton dynamics (formation, migration, capture and recombination) will most likely be forthcoming from non-linear and further linear optical experiments.

Apart from the added impact of nanofabrication upon the optical emission, there is evidence to suggest strain changes even in lattice matched structures. These will need particular attention as many of the device relevant materials are not lattice matched and/or include an alloy layer. The example of Si-SiGe demonstrates that strain relief due to nanopatterning into wires and dots is even stronger in strained material.

Finally, recent progress in the use of NSOM techniques opens the door for further understanding of optical processes in semiconductor nanostructures.

Acknowledgements

This work was supported by the UK Engineering and Physical Science Research Council under grant No. GR/J 90718, by the European Community ESPRIT program under project 6312 QUANTECS and by a NATO Linkage Grant No 921378. BBG and HFG thank the National Science Foundation for grant DMR-9158097 and the Sloan Foundation.>NNL thanks the Soros Foundation for financial support. HQ and FHP thank the National Science Foundation for grant No. DMR-9120363 and the Olympus Corporation. We thank C.R. Stanley and M.C. Holland for providing the GaAs-GaAlAs samples; T.E. Whall and E.H.C. Parker for providing the Si-SiGe samples; P.S. Kop'ev, V.M. Ustinov, and A.Yu. Egorov for their contribution to the preparation of the InAs-GaAs samples and I.N. Yassievich and A. Pakhamov for their calculations of the exciton binding energy in the InAs-GaAs samples. The technical support of A. Ross and H. McLelland is gratefully acknowledged. CMST acknowledges partial support from the Royal Society of Edinburgh.

References

- Alferov Zh, Egorov A Yu, Zhukov AE, Ivanov SV, Kop'ev PS, Ledentsov NN, Melt'er BYa, Ustinov VM (1992). Growth of GaAs-AlAs quantum clusters on non-(100)-oriented faceted GaAs surfaces by molecular beam epitaxy. *Sov Phys Semicond* **26**, 959-963.
- Arakawa Y (1994). Fabrication of quantum wires and dots by MOCVD selective growth. *Solid State Electronics* **37**, 523-528.
- Benisty H, Sotomayor Torres CM, Weisbuch C (1991). Intrinsic mechanism for the poor luminescence properties of quantum box systems. *Phys Rev B* **44**, 10945-10948.
- Betzig E, Trautman JK, Harris TD, Wiener JS, Kostelak RL (1991). Breaking down the diffraction barrier: Optical microscopy on a nanometric scale. *Science* **251**, 1468-1470.
- Bockelmann U (1992). Phonon scattering and relaxation properties of lower dimension electron gases. In: *Intersubband Transitions in Quantum Qells*. Rosencher E, Vinter B, Levine B (eds.). Plenum Press, New York. pp. 105-118.
- Bockelmann U, Bastard G (1990). Phonon scattering and energy relaxation in 2-dimensional, one-dimensional, and zero-dimensional electron gases. *Phys Rev B* **42**, 8947-8951.
- Bockelmann U, Egeler T (1992). Electron relaxation in quantum dots by means of Auger processes. *Phys Rev B* **46**, 15574-15577.
- Bockelmann U, Brunner K, Abstreiter G (1994). Relaxation and radiative decay of excitons in GaAs quantum dots. *Solid State Electronics* **37**, 1109-1112.
- Brandt O, Tapfer L, Cingolani R, Ploog K, Hohenstein M, Phillipp F (1990). Structural and optical properties of (100) InAs single-monolayer quantum-wells in bulk-like GaAs grown by molecular-beam epitaxy. *Phys Rev B* **41**, 12599-12606.
- Brandt O, Tapfer L, Ploog K, Bierwolf R, Hohenstein M, Phillip F, Lage H, Heberle A (1991). InAs quantum dots in a single-crystal GaAs matrix. *Phys Rev B* **44**, 8043-8053.
- Braslavets AV, Zhuravlev KZ, Moshegov NT, Toropov AI, Stenin SI (1991). Photoluminescence of $(\text{InAs})_n(\text{GaAs})_m$ superlattices under stress. *JETP Lett* **53**, 100-104.
- Bryant G (1992). Excitons in zero dimensional nanostructures. In: *Optics of Excitons in Confined Systems*. D'Andrea A, Del Sole R, Girlanda R, Quattropani A (eds.). Inst. Phys. (Bristol, U.K.) Conf. Series Vol. 123. pp. 131-138.
- Cingolani R, Brandt O, Tapfer L, Scarmacio G, La Roca GC, Ploog K (1990). Exciton localization in submonolayer InAs/GaAs multiple quantum wells. *Phys Rev B* **42**, 3209-3212.
- Clausen Jr E, Craighead HG, Worlock JM, Harbison JP, Schiavone LM, Florez L, Vand der Gaag B (1989). Determination of nonradiative surface-layer thickness in quantum dots etched from a single quantum well GaAs/AlGaAs. *Appl Phys Lett* **55**, 1427-1429.
- Darhuber AA, Koppensteiner E, Bauer G, Wang PD, Song YP, Sotomayor Torres CM, Holland MC (1995). X-ray reciprocal space mapping of GaAs/AlAs quantum wires and quantum dots. *Appl Phys Lett* **66**, 947-949.

- Dutta NK, Chand N, Lopata J, Wetzel R (1993). Temperature characteristics of $(\text{InAs})_1/(\text{GaAs})_4$ short-period superlattices quantum-well laser. *Appl Phys Lett* **62**, 2018-2020.
- Fahy MR, Dosanji SS, Dawson P, Joyce BA, Stradling RA, Murray R (1993). Incorporation of Silicon during MBE growth of GaAs on (11)A substrates. *J Cryst Growth* **127**, 871-876.
- Forchel A, Maile BE, Leier R, Mayer G, Germann R (1990). Optical emission from quantum wires. In: *Science and Engineering of One- and Zero-Dimensional Semiconductors*. Beaumont SP, Sotomayor Torres CM (eds.). Plenum, New York. pp. 277-295.
- Gerard M, Marzin J-Y (1988). High-quality ultra-thin InAs/GaAs quantum wells grown by standard and low-temperature modulated fluxes molecular-beam epitaxy. *Appl Phys Lett* **53**, 568-570.
- Ghaemi HF, Goldberg BB, Sotomayor Torres CM, Wang PD, Fritze M, Nurmikko A (1995). Spectroscopy of individual quantum structures with low temperature near field optical microscopy. *Superlattices and Microstructures*, **17**, 15-18.
- Goñi AR, Pinczuk A, Weiner JS, Calleja JM, Dennis BS, Pfeiffer LN, West K (1991). One-dimensional plasmon dispersion and dispersionless inter-subband excitations in GaAs wires. *Phys Rev Lett* **67**, 3298-3301.
- Greus Ch, Spiegel R, Faller F, Forchel A (1993). Lateral quantization effects in the optical properties of barrier modulated InGaAs/GaAs wires. *J Physique IV, Colloque 5, 3*, pp. 139-142.
- Gumbs G, Huang DH, Qiang H, Pollak FH, Wang PD, Sotomayor Torres CM, Holland MC (1994). Electromodulation spectroscopy of an array of GaAs/GaAlAs quantum dots: Experiment and theory. *Phys Rev B* **50**, 10962-10969.
- Grundmann M, Ledentsov NN, Heitz R, Eckey L, Christen J, Boehrer J, Bimberg D, Ruminov SS, Werner P, Richter U, Heydenreich J, Ustinov VM, Egorov AYu, Zhukov AE, Kop'ev PS, Alferov Zhi (1995). InAs/GaAs quantum dots: Radiative recombination from zero-dimensional states. *Phys Stat Sol (b)* **188**, 249-258.
- Ilg M, Nötzel R, Ploog K, Hohenstein M (1993). Morphology transformations of GaAs high-index surfaces during the initial-stages of strained layer overgrowth. *Appl Phys Lett* **62**, 1472-1474.
- Inoshita T, Sakaki H (1992). Electron relaxation in a quantum dot: Significance of multiphonon processes. *Phys Rev B* **46**, 7260-7263.
- Kapon E, Walther M, Hwang DM, Colas E, Caneau C, Bhat R (1993). Carrier capture and stimulated emission in quantum wire lasers grown on non-planar substrates. In: *Phonons in Semiconductor Nanostructures*. Leburton J-P, Pascual J, Sotomayor Torres CM (eds.). Kluwer, Dordrecht, The Netherlands. pp. 317-330.
- Kash K (1990). Optical properties of III-V semiconductor quantum wires and dots. *J Lumin* **46**, 46-82.
- Ledentsov NN, Wang PD, Sotomayor Torres CM, Egorov AYu, Maximov MV, Ustinov VM, Zhukov AE, Kop'ev PS (1994). Optical spectroscopic studies of InAs layer transformation on GaAs surfaces. *Phys Rev B* **50**, 12171-12174.
- Leitch WE, Sotomayor Torres CM, Lootens D, Thoms S, Van Daele P, Stanley CR, Demeester P, Beaumont SP (1992). Luminescence studies from wires of varying aspect ratio in GaAs-GaAlAs quantum wells. *Surf Sci* **263**, 622-627.
- Leonard D, Krishnamurthy M, Reeves CM, Denbaars SP, Petroff PM (1993). Direct formation of quantum-sized dots from coherent islands of InGaAs on GaAs surfaces. *Appl Phys Lett* **63**, 3203-3206.
- Leonard D, Krishnamurthy M, Fafard S, Merz JL, Petroff PM (1994). Molecular-beam epitaxy growth of quantum dots from strained coherent uniform islands of InGaAs on GaAs. *J Vac Sci Technol B* **12**, 1063-1066.
- MacLeod RW, Sotomayor Torres CM, Tang Y-S, Kohl A (1993). Carrier confinement and fabrication effects in GaInAs-InP quantum wires and dots. *J de Physique IV, Colloque 5, 3*, 335-338.
- Marzin J-Y, Gerald JM, Voisin P, Brum JA (1990). Optical studies of strained III-V heterolayers. In: *Strained Layer Superlattices: Physics, Semiconductors and Semimetals Series*. Vol. 32. Pearsall TP (ed.). Academic Press, New York. p. 55-118.
- Nötzel R, Ledentsov NN, Ploog K (1993). Confined excitons in corrugated GaAs/AlAs superlattices. *Phys Rev B* **47**, 1299-1304.
- Ploog K, Brandt O, Nötzel R (1992). Direct fabrication of III-V semiconductor quantum dots and quantum wires by molecular beam epitaxy. In: *Low Dimensional Electronic Systems*. Bauer G, Kuchar F, Heinrich H (eds.). Springer Series in Solid State Sciences vol. 111. Springer, Heidelberg, Germany. pp. 134-142.
- Qiang H, Pollak FH, Tang Y-S, Wang PD, Sotomayor Torres CM (1994a). Characterisation of process-induced strains in GaAs/Ga_{0.7}Al_{0.3}As quantum dots using room-temperature photorefectance. *Appl Phys Lett* **64**, 2830-2832.
- Qiang H, Pollak FH, Tang Y-S, Wang PD, Sotomayor Torres CM (1994b). Room-temperature characterisation of process-induced strains in GaAs/GaAlAs quantum dots. *SPIE Proc* **2139**, 234-240.
- Sela I, Watkins DE, Laurich BK, Smith DL, Subbana S, Kroemer H (1991). Excitonic non-linearity induced by internal field screening in (211) oriented strained-layer superlattices. *Appl Phys Lett* **58**, 684-686.
- Sotomayor Torres CM, Watt M, Arnot HEG, Glew

R, Leitch WE, Kean AH, Cusco Cornet R, Kerr TM, Thoms S, Beaumont SP, Johnson NP, Stanley CR (1990). Raman scattering and photoluminescence of GaAs-based nanostructures. In: *Science and Engineering of One- and Zero-Dimensional Semiconductors*. Beaumont SP, Sotomayor Torres CM (eds.). Plenum, New York. pp. 217-307.

Stern F (1992). Theory of electrons in low-dimensional systems. In: *Physics of Nanostructures*. Davies JH, Long AR (eds.). Institute of Physics Publishing, Bristol. pp. 31-52.

Tan I-H, Lishan D, Mirin R, Nayaraman V, Hu E, Bowers J (1991). Systematic observation of strained-induced lateral quantum confinement in GaAs quantum well wires prepared by chemical etching. *Appl Phys Lett* **59**, 1875-1877.

Tang Y-S, Wilkinson CDW, Sotomayor Torres CM, Smith DW, Whall TE, Parker EHC (1992). Fabrication and characterization of one dimensional hole gas. *Superlattices and Microstructures* **12**, 535-537.

Tang Y-S, Wilkinson CDW, Sotomayor Torres CM, Smith DW, Whall TE, Parker EHC (1993a). Optical properties of Si/Si_{1-x}Ge_x heterostructure based wires. *Solid State Commun* **85**, 199-202.

Tang Y-S, Wilkinson CDW, Sotomayor Torres CM, Smith DW, Whall TE, Parker E H C (1993b). Optical properties of Si/Si_{0.87}Ge_{0.13} multiple quantum well wires. *Appl Phys Lett* **63**, 497-499.

Wang PD, Sotomayor Torres CM, McLelland H, Thoms S, Beaumont SP, Wilkinson CDW, Kean AH, Stanley CR (1992a). Photoluminescence and Raman scattering studies of GaAs-AlGaAs quantum dots. *SPIE Proc* **1676**, 172-183.

Wang PD, Sotomayor Torres CM, Benisty H, Weisbuch C, Beaumont SP (1992b). Radiative recombination in GaAs-AlGaAs quantum dots. *Appl Phys Lett* **61**, 946-948.

Wang PD, Sotomayor Torres CM, McLelland H, Stanley CR (1993a). Photoluminescence intensity and multiple phonon Raman scattering in quantum dots: Evidence of the bottleneck effect. *Surf Sci* **305**, 585-590.

Wang PD, Cheng C, Sotomayor Torres CM, Batchelder DN (1993b). GaAs micrometer sized dot imaging by Raman microscopy. *J Appl Phys* **74**, 5907-5909.

Wang PD, Song YP, Sotomayor Torres CM, Holland MC, Lockwood DJ, Hawrylak P, Palacios JJ, Christianen JCM, Maan JC, Perenboom JAAJ (1994a). Optical emission and Raman scattering in modulation doped GaAs-AlGaAs quantum wires and dots. *Superlattices and Microstructures* **15**, 23-27.

Wang PD, Ledentsov NN, Sotomayor Torres CM, Kop'ev PS, Ustinov VM (1994b). Optical characterisation of submonolayer and monolayer InAs structures grown in a GaAs matrix on (100) and high index sur-

faces. *Appl Phys Lett* **64**, 1526-1528.

Wang PD, Ledentsov NN, Sotomayor Torres CM, Yassievicj IN, Pakhomov A, Egorov AYU, Kop'ev PS, Ustinov VM (1994c). Magneto-optical properties in ultrathin InAs-GaAs quantum wells. *Phys Rev B* **50**, 1604-1610.

Weisbuch C, Vinter B (1991). *Quantum Semiconductor Structures*. Academic Press, San Diego. pp. 189-215.

Yazawa M, Koguchi M, Hiruma K (1991). Heteroepitaxial ultrafine wire-like growth on GaAs substrates. *Appl Phys Lett* **58**, 1080-1082.