Self-Organized Quantum Dots

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Owing to their superior optical properties, uniform arrays of nanometre-sized buried quantum dots produced by self-organized growth are now the favoured option for applications in semiconductor devices.

Quantum semiconductor heterostructures have entered our daily lives. In every compact-disk player we find a quantum-well laser diode, and modern satellite television receivers rely on low-noise high-electron mobility transistors. These devices use the one-dimensional confinement of carriers to change the energy dependence of their density of states, from the square-root behaviour of the bulk to a step-like dependence for thin layers.

Advanced crystal growth techniques, notably molecular beam epitaxy (MBE) and metal-organic vapour phase epitaxy (MOVPE), make it possible to fabricate layered semiconductor devices such as heterojunctions, quantum wells and superlattices very precisely at the atomic scale. A further reduction in the dimensionality results in fundamentally new electronic properties in one-dimensional quantum wires and zero-dimensional quantum dots owing to the changeover of the energy dependence of the density of states – from a sawtooth behaviour in quantum wires to a singular behaviour for a quantum dot, the ultimate quantum confinement structure.

However, to exploit the electronic properties of zero- and one-dimensional structures in new types of high-speed, quantum interference and optoelectronic devices [1, 2], the lateral dimensions of the structures have to be in the range of, or smaller than, the de Broglie wavelength of electrons (50 nm in GaAs). Moreover, millions of the quantum structures, density packed and uniform on the atomic scale, are needed to achieve the appropriate active volume for practical applications. This calls for even more precise fabrication methods to provide improved control of the size and shape of large ensembles of nanostructures. Success here will not only allow improve performance, such as the ultra-low threshold current predicted for quantum-dot lasers [2], but also the realisation of novel device concepts, including the single-electron transistor.

Many attempts to fabricate quantum wires and dots have been reported for more than a decade. Methods have been mainly based on the lateral patterning of two-dimensional heterostructures, by combining fine-line lithography with wet and dry chemical etching, and on selective crystal growth on prepatterned and masked substrates [3]. However, it has turned out that in nanometre-scale structures where the size is directly related to the opening of lithographic patterns, shape irregularities and mechanical damage to interfaces cannot be avoided. So optical performance comparable or superior to that for quantum well structures has not been obtained.

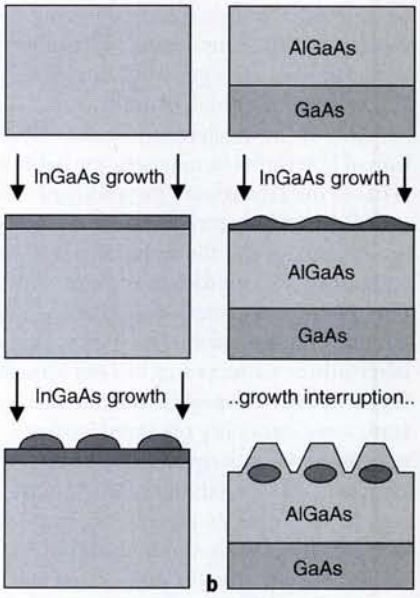

Fig. 1. Schematic illustrations of (**a**) the formation of islands in the Stranski-Krastanow growth mode; and (**b**) of the self-organizing formation of strained InGaAs quantum disks buried beneath AlGaAs nanocrystals on high-index substrates.

Lattice Mismatched Systems

Other approaches for producing low-dimensional nanostructures are therefore sought. Owing to its potential for creating damage-free structures [4], the direct synthesis of nanostructures during the epitaxial growth process itself has become very important. The formation of coherent islands during the heteroepitaxial growth of lattice mismatched systems (Stranski-Krastanow growth mode [5]) offers one method for making quantum dots [6].

Among the various combinations of III-V-semiconductors based on P or Sb compounds and Si SiGe alloys [7], the InGaAs/GaAs material system is the most widely studied. The strain that accumulates on growing a thin wetting layer of InGaAs is relieved by the formation of defect-free coherent InGaAs islands (dots) with diameters of 10-30 nm (Fig. 1a); further growth introduces defects in the dots.

The formation of coherent islands during MBE and MOVPE has been widely investigated [8], especially the growth conditions which are carefully adjusted in order to control the shape, size, density, and overgrowth of the dots [9]. Of special concern has been:

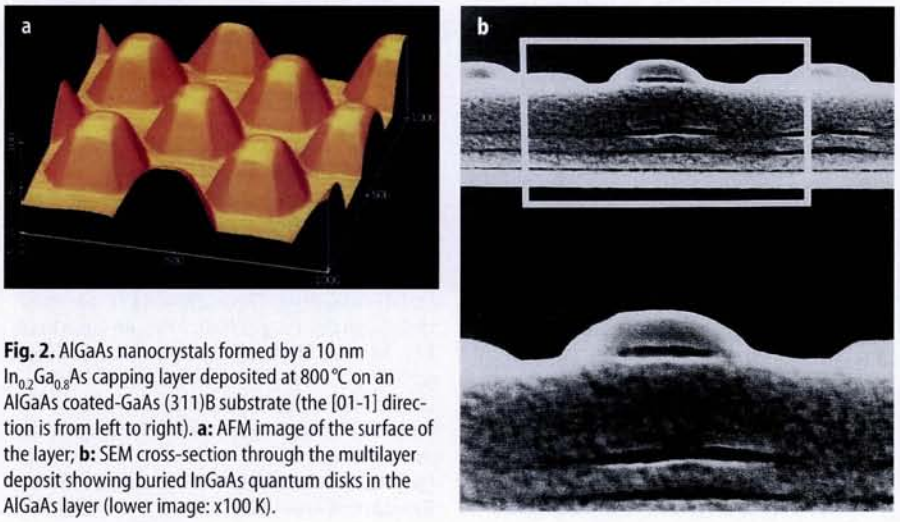

Fig. 2. AlGaAs nanocrystals formed by a 10 nm $In_{0.2}Ga_{0.8}As$ capping layer deposited at 800 °C on an AlGaAs coated-GaAs (311)B substrate (the [01-1] direction is from left to right). **a:** AFM image of the surface of the layer; **b:** SEM cross-section through the multilayer deposit showing buried InGaAs quantum disks in the AlGaAs layer (lower image: x100 K).

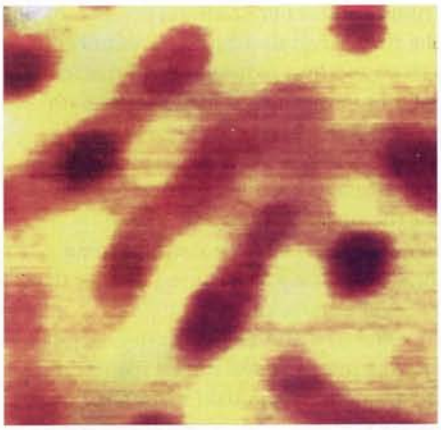

Fig. 3. AFM image of the modulated InGaAs surface after deposition of a 5 nm thick layer of $In_{0.2}Ga_{0.8}As$ at 750 °C on an AlGaAs-coated GaAs (311)B substrate. The total modulation depth is about 3 nm.

• vertical stacking of the dots due to strain fields during overgrowth [10];
• the possibility of lateral ordering owing to the preferential nucleation of dots at step edges [11];
• growth on patterned substrates [12];
• growth under the influence of lateral strain fields [13].

The charging of dots by individual electrons [14] and the generation of ultra-narrow lines in photoluminescence (PL) from single dots have been reported [15].

Up to now, however, it seems that the Stranski-Krastanow growth mode introduces unavoidable fluctuations in the size and shape of the dots, so a well-defined control of density and ordering is difficult to achieve. Moreover, the wetting layer inevitably connects the dots and optical properties have essentially not been improved since the first results: representative PL spectra remain much broader compared to those for quantum wells, and a good optical performance for buried InGaAs islands at room temperature – essential for practical devices – has yet to be reported.

Self-organized Quantum Disks

In seeking alternative techniques based on epitaxial growth, we discovered in 1993 a novel self-organizing growth mode for MOVPE on high-index (311)B GaAs substrates (B-type substrates are As-terminated while A-types are Ga-terminated). The new process overcame many of the difficulties associated with the direct synthesis of quantum-dot structures [16]. If the growth of an epitaxial InGaAs layer on an AlGaAs buffer layer is interrupted for a few minutes, the strained InGaAs layer arranges itself into nanometre-scale islands that are buried spontaneously beneath AlGaAs owing to lateral mass transport from the buffer layer (Fig. 1b).

This process, which does not occur on GaAs (100) substrates that are usually taken as the reference, forms well-ordered and high-density arrays of disk-shaped InGaAs dots inside faceted AlGaAs nanocrystals [16]. Self-organization during growth arises owing to a well-defined faceting and self-ordering of the AlGaAs nanocrystals, and to the complex processes that take place during the formation of the buried InGaAs/AlGaAs confined nanostructure. Features of the self-organized growth technique (see insert) demonstrate that the process can be controlled, applied to various materials systems and used to produce different types of structures.

The growth and optical properties of buried InGaAs quantum disks have been studied using thin layers grown on GaAs (311)B substrates at 700-800 °C in a low-pressure MOVPE reactor. Trimethyl alkyls of Ga, Al, In, arsine, and phosphine were used as source materials, with hydrogen as the carrier gas. After growth, samples were cooled at about 20 °C/min.

The following layer sequence was adopted for studying the growth process:

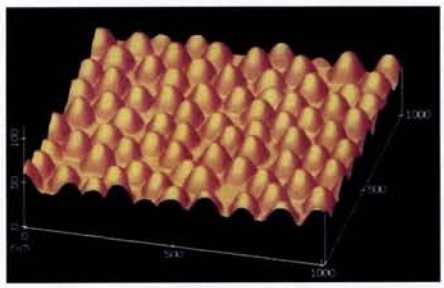

Fig. 4. AFM image of the AlGaAs nanocrystals formed by a 3.5 nm thick In0.4Ga0.6As layer deposited at 720°C on an AlGaAs-coated GaAs (311)B substrate showing the marked reduction in size resulting from an increased In concentration.

• three InGaAs layers with nominal In composition of 0.2 and thickness of 5 nm separated by 30 nm thick $Al_{0.5}Ga_{0.5}As$ buffer layers;
• a 100 nm thick Alo.5Gao.5As upper buffer layer ;
• a nominally 10 nm thick $In_{0.2}Ga_{0.8}As$ capping layer.

Growth at 800°C was interrupted for 10 seconds between the three InGaAs layers in order to partly suppress the formation of buried disks, thereby allowing the growth morphology to be monitored.

For optical measurements, an InGaAs layer was sandwiched between a 100 nm-

Features of Self-Organized Growth [18, 19]

• For InGaAs on GaAs substrates, the **size and separation** of quantum disks can be controlled independently within the mesoscopic size range (several 10 to 100 nm), without decreasing the uniformity in size and shape, by adjusting the In composition and the InGaAs layer thickness. Coupled quantum disks are obtained at a reduced growth temperature and/or a reduced InGaAs layer thickness or In composition, where lateral mass transport is hindered in order to maintain an uniformly modulated InGaAs layer.
• The formation of buried InGaAs quantum disks occurs not only on high-index GaAs (*n*11)B substrates, but also in GaInAs/AlInAs and GaInAs/InP material systems on **InP (311)B** substrates. For a similar lattice mismatch, the structures resemble those for the InGaAs/AlGaAs system on GaAs (311)B substrates (a 100 °C lower growth temperature compensates for the higher vapour pressure of In compared to that of Ga). So self-organized growth is common for strained layer growth on high-index semiconductor surfaces. (For A-type substrates, zero- and one-dimensional self-faceting by step bunching lead to wire-like nanostructures for GaAs (*n*11)A, and to dot-like nanostructures for GaAs (211)A.)
• The **surface morphologies** mirror directly the general features of the microscopic surface structures maintained during molecular beam epitaxy.
• The lateral periodicity of **self-faceting** of the embedded nanocrystals can be controlled by adjusting the layer thickness and the growth temperature, so the width of GaAs/AlGaAs (311)A wire-like heterostructures can be varied. The red shift of the photoluminescence from these quantum structures is directly correlated with the lateral periodicity of faceting.
• Buried InGaAs quantum disks also form on GaAs (211)B and (511)B substrates. Uniformity in size and ordering, however, are **optimum for GaAs (311)B**. This might be due to the nominal composition of (311) planes, where equal amounts of high-symmetry (100) and (111) planes provide the highest degree of anisotropy for surface migration as well as the atomic configuration needed for self-ordering.
• GaInAs layers grown directly on InP buffer layers develop buried nanostructures for both compressively and tensile **strained layers**, but exhibit much less pronounced faceting and ordering than for tensile strained $Ga_{0.75}In_{0.25}As$ layers, where a rough surface is formed.

thick lower and a 50 nm-thick upper AlGaAs barrier layer, with a growth interruption time of 3 minutes to promote complete self-organization. High-resolution scanning electron microscopy and atomic force microscopy confirmed that the morphology of the buried InGaAs layer in this sample was the same as that observed in the other types of samples.

Growth studies

A three-dimensional atomic-force microscope (AFM) image of the surface of the $In_{0.2}Ga_{0.8}As$ capping layer is shown in Fig. 2a (the [01-1] direction is from left to right in all AFM images). An array of well-ordered nanocrystals with a faceted surface is clearly resolved [17]. This ordering may have resulted from the strain-induced breaking up of the InGaAs layer combined with the appearance of the crystal facets on the AlGaAs nanocrystals, The facets led to the selection of specific directions for surface migration during the formation of the buried InGaAs structure.

The structure of the AlGaAs nanocrystals with their enveloped InGaAs disks is resolved in Fig. 2b giving a cross-sectional scanning-electron microscope (SEM) image of the buried quantum disks in the same sample as Fig. 2a (the image is viewed along the [01-1] direction). The darker regions correspond to InGaAs and the lighter ones to AlGaAs. The nanocrystals are composed of disk-shaped InGaAs dots with a diameter of about 150 nm embedded in an AlGaAs matrix with a thickness of about 30 - 40 nm. Since no AlGaAs was deposited after the last InGaAs layer, this structure implies that the InGaAs layer broke up into isolated islands following deposition: the islands were buried spontaneously beneath AlGaAs nanocrystals owing to lateral mass transport from the buffer layer [16].

The dynamics of the growth process were revealed by changes in the structure of the three InGaAs layers contained within the AlGaAs buffer layer (the morphology of each layer is quenched in at an intermediate stage owing to the overgrowth of AlGaAs after the 10 s growth interruption). The first InGaAs layer was very uniform in thickness, suggesting that islanding and lateral mass transport took place on a time scale between several seconds (growth interruption time) and several minutes (cooling time). However, the disk-like morphology of the second and third InGaAs layers shows the rate of formation of the InGaAs disks was enhanced by surface waves and strain fields introduced by the overgrowth of a strained layer. Moreover, the cross-sectional SEM image indicated that the disks could be stacked in the vertical (growth) direction, with disks in a lower layer initiating the formation of disks in the next layer due to the generation of strain.

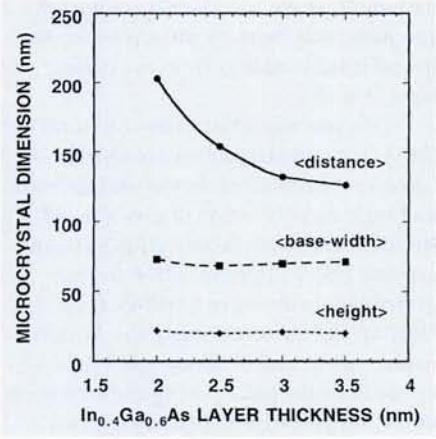

Fig. 5. The distance apart , base width and height, plotted as a function of the InGaAs layer, of the AlGaAs nanocrystals formed by a 3.5 nm $In_{0.4}Ga_{0.6}As$ layer deposited at 720°C on an AlGaAs-coated GaAs (311)B substrate.

An InGaAs layer with uniform thickness modulation must be grown during the initial stage of growth in order to produce a uniform array of quantum dots. It has been shown that uniform modulation requires a reduced growth temperature and/or InGaAs layer thickness or In composition [18]. Fig. 3 gives an AFM image of the modulated surface of a 5 nm thick $In_{0.2}Ga_{0.8}As$ layer grown at 750°C. Break-up of the layer and lateral mass transport from the buffer layer are suppressed by the reduced strain energy for thinner layers, and by a reduced rate of surface migration distance at the lower growth temperature. A very uniform array of coupled quantum dots arises if growth is interrupted for 3 minutes before depositing the AlGaAs upper buffer layer (coupling may be important for some applications, *e.g.*, measuring devices that need an electric current).

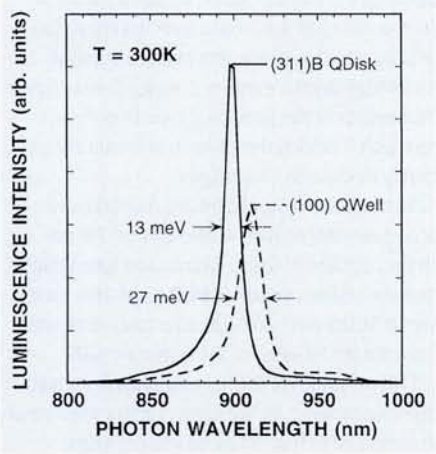

Fig. 6. Comparison between the photoluminescence spectrum at room temperature of a (100) quantum well, which is taken as the reference, with the spectrum for a buried quantum-disk structure, generated using a nominally 5 nm thick $In_{0.25}Ga_{0.75}As$ layer grown on a GaAs (311)B substrate,

The sizes of the AlGaAs nanocrystals and the InGaAs disks can be reduced by increasing the nominal In composition owing to the smaller island size at higher strains [17]. Fig. 4 shows a three-dimensional AFM image of an array of AlGaAs nanocrystals formed using a nominally 3.5 nm thick $In_{0.4}Ga_{0.6}As$ layer grown at 720°C (the scale is the same as for Fig. 2a). The width of the base of the nanocrystals is 70 nm, corresponding to the diameter of the inner InGaAs disks – 20-30 nm and well within the quantum-size regime. More importantly, shape uniformity, the shape itself (*i.e.*, the ratio of height to the width of the base) and ordering are maintained upon size reduction.

Growth mechanism

The experimental results suggest that the formation of the buried disks can be described in terms of a complex interplay between surface energy, strain and surface migration. Surface waves or islands reduce the total energy of the strained InGaAs layer. However, the tendency to form islands is suppressed at an early stage owing to a high-energy barrier for adatom migration, where an initially higher surface energy for (311)B planes compared to (100) planes may lower the energy barrier thereby accelerating the break-up of the InGaAs layer. The high substrate temperature then allows material from the buffer layer to bury the InGaAs islands to form an unstrained surface with facets of low surface energy. The rate of formation of the buried InGaAs disks is therefore enhanced at higher substrate temperatures and/or higher strain energy for thicker InGaAs layers or a higher In composition.

The separation into AlGaAs nanocrystals (each having an embedded InGaAs disk) is determined by the nominal InGaAs layer thickness. This can be seen in Fig. 5 which plots the average separation, base width, and height of the AlGaAs nanocrystals as a function of the nominal thickness of the InGaAs layer for a fixed In concentration. The average separation of the nanocrystals decreases with increasing

InGaAs layer thickness, while the average base width and height remain almost unchanged. Since the average separation of the nanocrystals does not depend on the In composition, the size and separation of InGaAs quantum disks can be adjusted independently, without changing the crystal shape, by varying the In composition and the InGaAs layer thickness .

Optical properties

The photoluminescence (PL) linewidth at cryogenic temperatures of the InGaAs disks is comparable to, or smaller than, the width for the reference (100) quantum wells. So inhomogeneous broadening due to size fluctuations of the dots is comparable to that of state-of-the-art quantum wells.

Fig. 6 compares a PL spectrum at room temperature for nominally 5 nm thick $In_{0.25}Ga_{0.75}As$ disks (lateral size of 60 - 70 nm) with the spectrum for a reference quantum well grown at 750°C. Strikingly, the linewidth for the disks is only 13 meV [20]. This small linewidth indicates that the interfaces of the disks are smooth and ordered. The opposite is the case for islands formed in the Stranski-Krastanow growth mode, where PL line broadening is always observed. Moreover, the narrow linewidth indicates reduced thermal broadening, thus confirming the efficient lateral confinement and localization of the photogenerated carriers inside our quantum disks. This first experimental evidence for strong confinement and localization in quantum dots at room temperature highlights the opportunities presented by self-organized growth for obtaining nanodevice-quality structures.

The PL efficiency at room temperature is comparable to that of the reference quantum wells for all buried disk structures, isolated or coupled, and the PL linewidth is not increased relative to that of the wells, even for the disks with an average diameter of 20-30 nm. So strained quantum disk lasers operate in the continuous-wave mode at room temperature with a threshold current that is about 1.5 times less than that of a conventional (100) quantum well laser [21].

Further Developments

Application of the self-organizing growth of buried InGaAs quantum disks calls for further improvements in techniques to adjust the size, shape and lateral positioning of nanostructures formed on high-index surfaces [16]. The additional control that arises if high-index substrates are patterned is one option, because the unique growth mechanism suggests that novel phenomena may arise.

Recent studies of the selectivity of growth on patterned GaAs (311)A substrates by MBE have indeed shown that new possibilities exist. A fast-growing sidewall was observed along one side of a raised stripe (a so-called mesa) oriented in the [01-1] direction. Preferential migration of Ga atoms to the sidewall took place from the top of the mesa and from the surface of the surrounding substrate, *i.e.*, in directions opposite to those for patterned (100) or (111) substrates. This led to a stable mesa–substrate junction and an unfaceted sidewall with a smooth convex profile. Buried quantum wires, some 10 μm long and with a self-limiting width, could then be produced along the sidewall, even for mesa heights that were on the quantum-size scale [22].

It has also been found very recently that InGaAs islands can be grown on the top of the mesa and on the surrounding substrate, while keeping the curved sidewall island-free. So patterned substrates will probably lead to techniques for positioning quantum dots, a feature which is required in many applications.

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