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Quantum Dot Structures in the InGaAs System Investigated by TEM Techniques

Dedicated to Prof. Dr. J. Heydenreich on the occasion of his 70th birthday

Quantum dot structures have gained increasing interest in materials science due to their special electrical and optical behavior. A combination of electron-optical techniques is applied to correlate such properties with the morphology and structure of quantum dots in the InGaAs system. TEM techniques, e.g. imaging by conventional diffraction contrast, by high-resolution TEM and by energy filtering (EFTEM) are focused on the determination of parameters, like shape and size of islands, their chemical composition and the complex lattice strain fields. An image contrast analysis in terms of shape and strain demands the application of image simulation techniques based on the dynamical theory and on structure models refined by molecular dynamics or molecular static energy minimization.

Keywords: : quantum dots, InGaAs, Transmission Electron Microscopy, crystal structure

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1. Introduction

The investigation of semiconducting nanostructures is especially focused on the properties of so-called quantum dots (QD), which are embedded in a different semiconducting bulk or in other materials. The possibility of arranging such particles or "dots" into complex arrays implies many opportunities for scientific investigations and technological applications. Over the last 10 years, various ways have been applied successfully to create semiconductor particles of several 10 nm in size, evidencing special properties to be different from the bulk behavior (for an overview see, e.g., MRS Bulletin). In the field of basic physics, QDs represent a striking subject for studying effects in quantum physics, in 'single electron' and laser physics (WEISBUCH et al.).

Concerning their technological application, QD structures are most attractive for active as well as passive optoelectronic devices (e.g., vertical cavity surface emitting lasers, VCSELs). There was a breakthrough, when it became possible to create high-density arrays of QDs by the epitaxial growth of lattice mismatched heterostructures ("Stranski-Krastanow" growth mode) such as vertical-stacked InAs islands on a GaAs substrate. Depending on the growth techniques applied (mainly MBE and MOCVD), the islands differ in size, shape, chemical composition and lattice strain. All these parameters strongly influence the optical properties of such complex quantum structures (see, e.g., BIMBERG et al.). Therefore, a detailed knowledge of the growth, especially the interaction between kinetic processes and thermodynamics is necessary. The following methods of investigation have been applied successfully: photoluminescence (PL), cathodoluminescence (CL), X-ray diffraction, atomic force microscopy (AFM), techniques of transmission electron microscopy (conventional TEM, HREM), including energy-filtered TEM (EFTEM). In addition, the modeling and simulation of quantum structures and corresponding TEM images are necessary for a successful interpretation of experimental data. The paper presents some survey of the possibilities and limitations of TEM methods. It should be pointed out, however, that only some combination of the above-mentioned techniques allows the successful morphological analysis of QD structures, their growth phenomena and optical behavior.

Fig.1 presents some basic features of the formation of InAs dots/islands on a GaAs substrate grown via the "Stranski-Krastanow" mode obtained from TEM investigations. The first deposited monolayers (ML) create a pseudomorphous closed layer (wetting layer, WL), which is strained due to the lattice misfit (7% for InAs/GaAs). During a further deposition (≈2ML) small islands are forming (b). This transition from the layer growth to the island formation results from a complex process, which includes lattice strain and kinetic processes like surface diffusion and the incorporation of ad-atoms. As an example, TEM investigations have shown that specific growth interruptions (few seconds to some minutes) cause island growth and a consumption of WL material around the islands (Figs.1b - c) (SCHMIDT K.H. et al.).

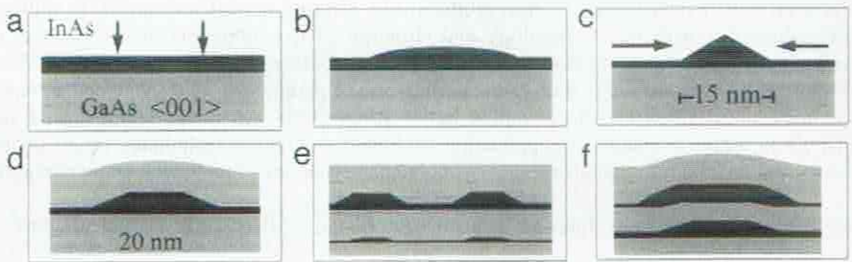


Fig. 1: Scheme of different growth steps of the island formation in the lattice-strained InAs/GaAs system: a) pseudomorphous layer growth up to about 1.7 ML, b) island formation for >1.7 ML deposition, c) pyramid formation due to surface diffusion, d) embedded InAs island, e) size and density of islands increase by a thin "seeding" layer, f) vertical stacking of QDs.

The interaction between surface strain fields and growth energetics is predicted to improve the lateral ordering (TEICHERT et al.). Owing to the growth parameters and techniques applied, different shapes of islands occur varying between flat pyramids and spherical islands. During further growth, the islands are usually covered with a GaAs coating/capping layer. As a result of a complex diffusion process the island shape is transformed, for instance, into a truncated pyramid (Fig. 1d). While AFM investigations show only a specific situation of the islands at the surface, TEM enables one to correlate optical measurements with structural features. To increase the size and density of QDs different techniques have been developed successfully, e.g, stacking of islands (cf. Fig. 1f) or to use a thin seeding layer, which is slightly corrugated.

For the InGaAs system, the scientific interest and technological aim is focused on QD arrays emitting light of about 1.3 to 1.5 μm, depending on the following parameters of the QDs: size, shape, lattice strain and chemical composition. All these specific parameters are combined in a complex way due to the thermodynamics and kinetic processes during the growth of QD samples. It is the aim of TEM techniques to separate these parameters of complex information, e.g., strain and chemical composition. This paper presents examples of TEM investigations of embedded InGaAs islands in a GaAs matrix and their correlation with corresponding simulated structures.

First, the problem of the determination of the size and the shape of islands is discussed. The second part deals with the analysis of the chemical composition with a lateral resolution in the nanometer range. For a detailed characterization of islands, corresponding structure simulations are necessary including the role of the 3-dimensional lattice distortion. Such simulations are discussed in the third part. Finally, investigations of multiple-stacked QD structures are presented, which are of physical and technological interest.

2. Determination of size and shape

Due to the lattice mismatch between an island and the surrounding matrix such a region is 3-dimensionally strained. HREM images can yield only a rough estimate of the shape and the crystallography of the interface (if sharp interfaces exist at all). Fig. 2 shows a typical plan-view TEM image of InAs dots on a GaAs substrate. Due to the conventional diffraction contrast technique applied the dots are mainly detectable by their strain fields. From contrast analyses it can be concluded that the dots seem to have a quadratic base face and edges along <100> directions. Such images allow one to determine not only the size distribution (see upper right) and dot density (here about 10^{11} cm^{-2}), but also the relation between adjacent islands. In this particular case, the islands have distances of about 25 nm and are preferentially arranged in specific crystallographic directions.

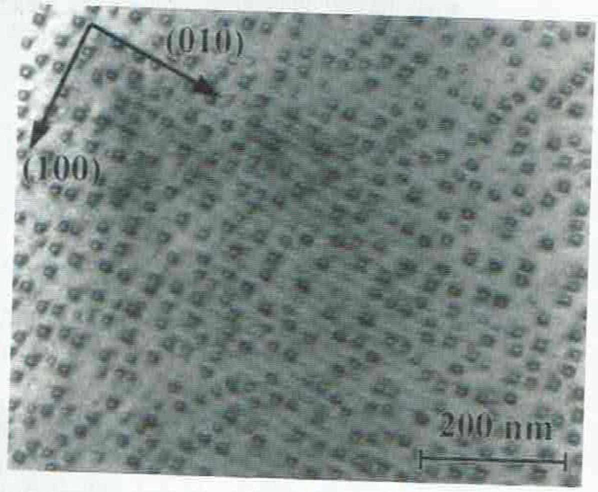
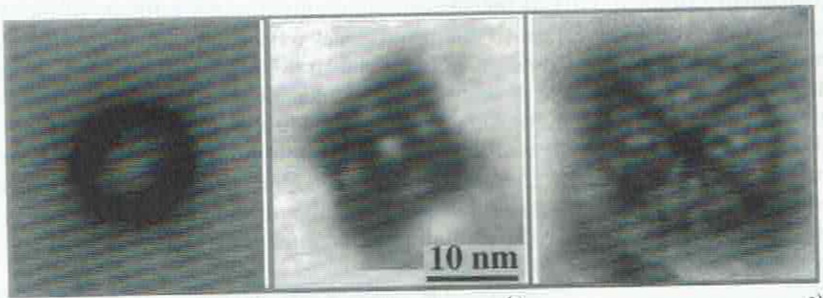


Fig. 2: Bright-field TEM image of a single layer of InAs dots grown on a (001) GaAs substrate by MBE. The specimen is exactly orientated in <001> orientation to get appropriate imaging conditions.

In bright-field TEM images, islands of a single dot layer sample often appear as dark contrast dots having a bright center. This contrast, mainly caused by the strain field, correlates to the size of the islands, however, the exact size and shape of their bases cannot be determined easily. Different attempts have been made to gain this information by comparing the experimental images with the simulated contrasts based on specific island models. A careful analysis of bright-field TEM contrasts revealed that, under special growth conditions, the islands may have the shape of a lens with a circular base (ZOU et al.). In other experiments, the dots seemed to have a more rectangular or rhombohedral base (see also Fig. 3).

Size and lattice strain of a QD are always correlated, and the question arises if both components can be separated by TEM techniques, which has been tried several times recently by comparing experimental images with the simulated contrast of model systems. One attempt was concerned with the calculation of strain fields of a given QD model (shape, chemical composition) using, e.g., the "finite element" approach (CHRISTIANSEN et al., GRUNDMANN et al.) or "molecular dynamics" structure calculations (MD) (RUVIMOV et al.). Fig. 3 shows bright-field images of different QDs taken in in-zone <001> orientation. Figs. 3a and b represent samples of InGaAs islands grown under different conditions. It seems that for single QD layers (a) the islands are smaller and have circular bases, whereas in the case of multiple-stacked layers (b) the QDs are getting larger, with flat facets and strain causing the typical 'cross' contrast features. Their base seems to be more quadratic or rhombohedric. Such a contrast behavior is more pronounced for uncapped islands, such as demonstrated for an uncapped Ge island grown on a Si substrate (Fig. 3c). Corresponding cross-section images show that in most cases the islands (from a single layer) are flat, and in the case of pyramids, mostly have a truncated shape.



a) b) c)

Fig. 3: Bright-field plan-view images of QDs of different samples.
a) a capped InAs island of a single QD layer,
b) a larger island formed in a multiple-stacked layer,
c) an uncapped Ge island.

3. Determination of Chemical Composition

Beside on size and shape, the energy states of the excitons depend on the local chemical composition inside the islands. It is influenced, e.g., by the growth process and the post-growth annealing of the samples implying an interdiffusion of the elements between matrix and island. The change in stoichiometry as, for instance, the In/Ga ratio is revealed as an integral measurement using PL spectroscopy. Several approaches have been made to determine an element distribution in the sub-nm-range by image processing of HREM micrographs (see, e.g., THOMA, OURMAZD, ROSENAUER, STENKAMP). In most of them the image analysis is carried out cell-wise to map the chemical composition in each projected specimen cell. Alternatively to these approaches (OURMAZD et al.), composition profiles at III-V interfaces were interpreted by a fuzzy logic approach (HILLEBRAND et al.). The local composition in the HREM image is concluded by a fuzzy logic rule base evaluating the template similarities related. In a neural network based method (HILLEBRAND et al.) experimental images of III-V layer structures are analyzed by feed forward networks being trained with simulated patterns including amorphous noise.

The application of these techniques to the analysis of QD structures is partly restricted. Hence, first one has to separate/eliminate lattice distortions, which would disturb the analyzing process. Therefore, a general problem of HREM image analyses is the separation of imaging parameters to gain independent information of them. This includes the determination of the local specimen thickness, imaging parameters as well as lattice strain fields. Fig. 4 demonstrates the situation of a single layer of InGaAs dots grown by MOCVD (ZAKHAROV and SELLIN et al.), where the In distribution has been analyzed in the island as well as in the InAs wetting layer. The upper part shows a cross-section image of the island at lower magnification. Two sections (circles) have been analyzed by image processing of the corresponding HREM micrograph (middle). The information of the chemical composition has been derived from analyzing the (002) reflected beams, which are chemically sensitive to the share of different atomic species in the zinkblende sublattices for crystallographic reasons. Due to the complex lattice distortion at the islands the accuracy and the local resolution of this method is restricted (in this case: 10%). However, it is obvious that within the island the In concentration is shifted to the upper region (maximum 40%). Furthermore, the In in the surrounding wetting layer is consumed during the further growth of the island caused by a post-annealing step. Such an interdiffusion-related changing of size and stoichiometry of islands has a direct influence on the emitted wavelength detectable by PL measurements.

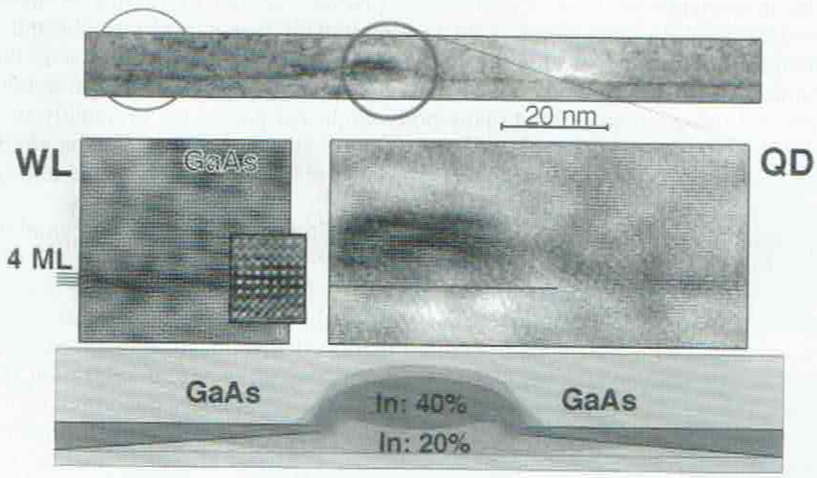


Fig. 4: Analysis of a single layer of InAs QDs. Upper part – cross-section image.
Middle part – HREM image of the wetting layer (WL) consisting of 4 monolayers of InAs. Lower part – scheme of the inhomogeneous In distribution in the island. The chemical analysis (distribution of In) is obtained from image processing ({200} filtering).

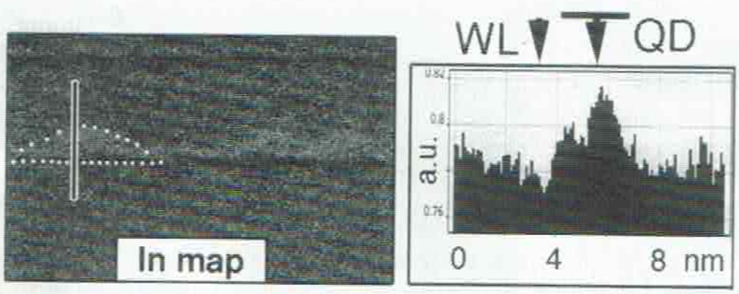


Fig. 5: EFTEM image of a single InAs dot layer using the In signal (left). The corresponding line scan (right) indicates an inhomogeneous In concentration in the island in growth direction.

Besides HREM image analysis, energy-filtered TEM has become well-established in recent years allowing chemical mapping with a lateral resolution down to the 5 Å range. In such element-specific images even single lattice planes are resolved. However, also in this case lattice strain fields have to be taken into account for a quantitative interpretation of the chemical distribution (SCHNEIDER et al.). Fig. 5 presents such an EFTEM micrograph of a single InAs dot layer grown by MBE. The In element map is shown on the left, where the position of the island is marked by dots. The line scan on the right shows the presence of In in the region of the island, where a higher In content was identified especially at the top of the QD marked by an arrow. Such an inhomogeneous In distribution occurs particularly in larger InAs/InGaAs dots.

4. Simulation of QD Structures

4.1. Structural Modeling

While, in principle, it is now possible to predict material properties by using quantum-theoretical ab-initio calculations with a minimum of free parameters, the only method of simulating time-dependent atomic processes with macroscopic relevance is the molecular dynamics (MD). This method bases on solving Newton's equations of motion for a molecular system and using suitably fitted many-body empirical potentials, preferably of the Tersoff-bond-order type (CONRAD et al., SCHEERSCHMIDT et al.). The calculations are done using a constant volume (NVE ensemble) or a constant pressure (NpT ensemble) and time steps of the order of 0.25 femto seconds.

Alternatively to MD for structures near the equilibrium, static energy minimization may be performed using steepest descent or conjugate gradient methods to relax the structures towards one of the nearest local energy minima. In Fig. 6, typical structure models are shown (Fig. 6a: examples of pyramids with facets {011}, {112}, {113}, and {136}, Fig. 6b: complete model with embedded pyramid, Fig. 6c: HREM image simulations before and after relaxation, respectively) to demonstrate the striking influence of relaxation on the image contrast. The relaxation was calculated under periodic boundary conditions at the side faces of the GaAs supercell, with the InAs pyramids inside (for details see a forthcoming paper or the application to the CdZnTe system, SCHEERSCHMIDT et al.). Nevertheless, the difference of the energy before and after relaxation is rather small, the different wetting layers, truncations, and step structures of the facets varying due to their different inclinations, yield characteristic strain fields.

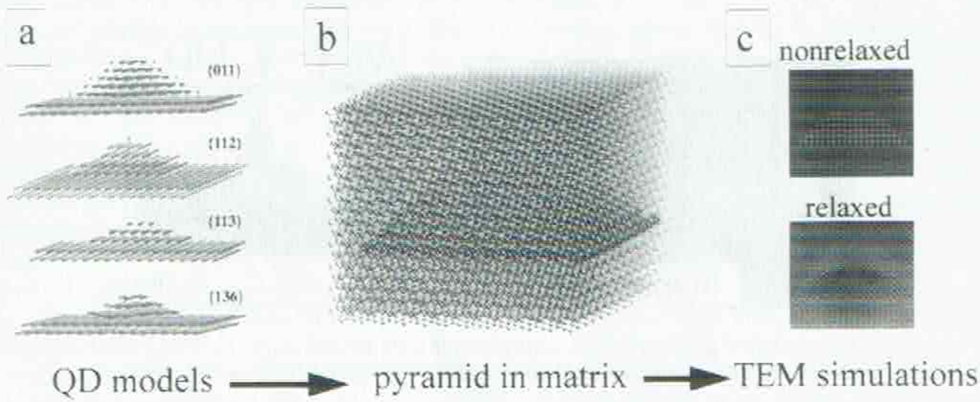


Fig. 6: Scheme of simulated pyramidal-shaped InAs QDs in GaAs after applying MD-relaxations. a) Different models of pyramids analyzed including different facetting, wetting and truncation (matrix removed). All models are related to a (001) base plane. b) Complete atomic model, {011} facets. c) HREM images of QDs before and after relaxation, respectively (TEM parameters: 400 kV, spherical aberration C_s = 1 mm, thickness t = 9 nm, Scherzer focus Δf =40 nm).

4.2. Image Simulations

The simulation of the image contrast of such models might be performed via multi-slice calculations, starting with MD relaxed supercells, which are sliced so that at least 4 sub-slices per unit cell in <100> direction are used. The imaging parameters are chosen according to a microscope experimentally used for high resolution microscopy (Jeol JEM 4000EX, accelerating voltage U = 400 kV, spherical aberration C_s = 1.2 mm, defocus spread Δf = 8 nm, and beam divergence α = 0.05 mrad). The imaging aperture is varied between 2 nm^{-1} and 6 nm^{-1} to have sufficient information of the QD itself and to avoid image artefacts.

Fig. 7 shows simulations of pyramidal QDs of the {011} type (a) in comparison with QDs shaped as spherical segments (b) for a different sample thickness, depths and defect sizes to characterize the contrast variations. This simulation demonstrates that, under appropriate imaging and specimen conditions, it is possible to get some information on the shape of grown island, especially to distinct between different QDs by their characteristic contrast details caused by their strain fields.

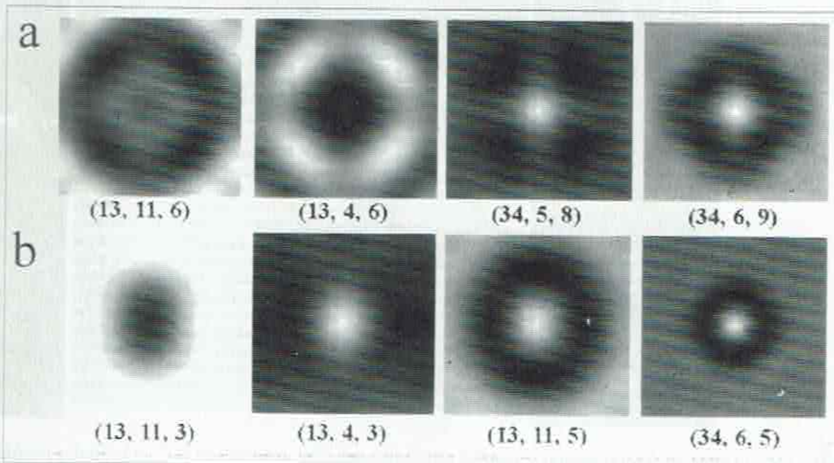


Fig. 7: Simulated 400 kV bright-field diffraction contrast TEM images of {011} pyramids (a) and spherical segments (b) for different thickness t, depth t_o of the QD below the surface and defect sizes d, characterizing the base length of the pyramid or the base diameter of the segments, given as approximated parameter set by (t/nm, t_o/nm, d/nm) below each pattern.

5. Three-Dimensional QD Structures

Optical properties of a single QD layer are characterized by a broad PL peak, which is related to the size distribution of QDs. To improve this situation (higher dot density, more pronounced size distribution) promising solutions have been developed, two of which will be mentioned. First, multiple stacking of QD layers has been envisaged as an attractive growth concept to provide a 3-dimensional array of islands. The short vertical distance of such layers of several nm generates an electronic coupling between adjacent islands and opens a way to tailor the wavelength of the emitted light. This multiple-stacking growth concept has successfully been applied to several systems of semiconductors (TERSOFF et al., HEINRICHSDORFF et al.).

One starts with a first QD layer, which is then covered with a GaAs capping layer. Next, about 2 ML of InAs are deposited. Due to surface diffusion, the first QD is covered with GaAs, with a second QD layer forming. In the case of <001> oriented substrates, the interaction between adjacent layers due to lattice strain variations induces a vertical alignment of islands. Fig. 8 shows a cross-section image of such a "self-ordered" assembly of InAs islands in GaAs. The micrograph demonstrates: i) the island size increases with the number of layers, ii) an improvement of the narrow size distribution, iii) a flattening of the growth surface by the GaAs spacer, especially for MBE grown samples. The strong periodicity of the layers in the vertical direction is proven by the occurrence of satellite reflections near the main reflections in the SAD pattern (left). The horizontal periodicity of QD is revealed by subreflections in the corresponding diffractogram (Fourier transformation, right). The first layer of InAs deposited is characterized by small flat islands (cf. schematic diagram of Fig. 1). Their homogeneously distributed strain fields cause the InAs islands to grow in size.

Fig. 8: Cross-section image of a multiple-stacked array of 25 InGaAs QD layers (dark islands) in a GaAs matrix (grey). The strong periodicity of the QD array is represented by subreflections in the SAD pattern (left) and the FFT diffractogram (right).

In such stacked QD layers, excitons are not only localized at a single island, but at several adjacent ones. PL and CL measurements have shown that such arrays are characterized by a strong electronic coupling. This behavior allows not only an emission (lasing) at room temperature but a tailoring of the emitted wavelength due to a quantization in 'larger volumes'. To improve the homogeneity of the QD size and density, further growth concepts have been developed, for instance, the island growth on vicinal surfaces, or the use of sub-MLs of InAs as seed layers for the subsequent conventional island growth (see Fig. 1).

Recently, a further possibility for attaining an emission for longer wavelength (> 1.3 μm) has been demonstrated by generating laterally associated QDs (MAXIMOV et al.). Different to growth procedures described above, InAs is deposited at lower substrate temperatures, i.e. in the range between 300 and 400 °C. TEM plan-view as well as cross-section images show that the dot size is decreasing with decreasing temperature, whereas the island density is increasing. Furthermore, QDs are arranged as complex arrays of laterally linked islands containing 3 to 10 dots. There are several other attempts to increase the dot density, the homogeneity of the distribution of the islands as well as the size distribution.

6. Conclusions

Electron-optical methods have been preferentially applied to characterize the structure as well as the chemical composition of QDs. Besides imaging techniques, which have been interpreted on the basis of image simulations and image processing, spectroscopic methods, such as PL and CL, yielded clear evidence of quantum effect based emission of such nanostructure assemblies. In the InGaAs system islands have a size of about 20 nm, however, the base shape (quadratic, circular) strongly depends on the particular growth conditions. Larger islands, especially such in multiple-stacked columns, have the tendency to form pyramids, whereas small islands in single layers show a flat shape with a circular character. Nevertheless, strain and chemical composition of islands can be successfully separated when applying imaging under different conditions. As an example, cross-section HREM micrographs are sensitive to lattice strain in <011> image projection, whereas <100> oriented images are appropriate for a chemical analysis.

With the complexity expected of 3-dimensional QD structures, advanced TEM techniques (HREM, EFTEM), but also diffraction contrast TEM in combination with the above-mentioned analytical methods (PL, CL) play an essential role in correlating the morphology and structure with the optoelectronic properties of semiconducting QD arrays. Structural as well as chemical analyses in the nm-range by HREM/EFTEM are not restricted to islands of III-V/II-VI semiconductors. It is also applicable to group-III nitride-related quantum structures and SiGe heterostructures (ABSTREITER et al., SCHMIDT O.G.). Recently, the incorporation of InAs dots in a Si matrix was successfully demonstrated (ZAKHAROV et al.). This might open the combined use of optoelectronic materials with integrated circuits based on the Si technology.

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