Self-ordering in CdSe/ZnSe, CdSe/(Zn,Mn)Se, InSb/GaSb, and InSb/InAs quantum dot structures and a novel type of quantum dot

Peter Möck1*, Teya Topuria1, Nigel D. Browning1, Graham R. Booker2, Nigel J. Mason3, Robin J. Nicholas3, Lubov V. Titova4, Malgorzata Dobrowolska4, Sanghoon Lee4, and Jacek K. Furdyna4
1 Department of Physics (MC 273), University of Illinois at Chicago, 845 W. Taylor Street, Chicago, IL 60607-7059, U.S.A; *pmoecck@uic.edu
2 Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, U.K.
3 Department of Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, U.K.
4 Department of Physics, University of Notre Dame, Notre Dame, IN, 46556, U.S.A.

ABSTRACT
CdSe quantum dots (QDs) in a ZnSe matrix, quasi-2D CdSe platelets in a (Zn,Mn)Se matrix, and InSb QDs in InAs and GaSb matrices are characterized by transmission electron microscopy (TEM) in the scanning electron-probe and the parallel-illumination modes. A phenomenological scheme of self-ordering of QDs from the literature is used as a tool for the classification of laterally self-ordered arrangements of these QDs and their predecessor islands. Modified growth conditions led in all studied cases to self-ordered QD and island arrangements of higher levels. CdSe and InSb rich agglomerates of varying sizes (approximately 5 nm to a few 100 nm) with different types of internal compositional modulation have been formed by self-ordering on an atomic scale, potentially forming a new type of QDs and suggesting that the self-ordering process may be of a dissipative nature.

INTRODUCTION
“Paradigm changes in semiconductor physics” [1] are expected to emerge from research into self-assembled semiconductor quantum dot structures (QD). The required high uniformity of the shape, size, and alignment of QDs that may make them employable as active media in novel opto-electronic devices is thought to be achievable by means of self-ordering processes during Stranski-Krastanow growth. Theoretically founded schemes of self-ordering are needed for the experimentalist to classify the observed QD arrangements before and after modifications of the growth conditions in order to judge the effectiveness of the latter. To our knowledge, there is at present only one phenomenological classification scheme for lateral self-ordering of QDs [2] available and the nature of the ongoing self-ordering processes [3] has not been precisely clarified. In this paper, we will apply this phenomenological scheme as a tool in order to demonstrate the effectiveness of modified growth conditions for CdSe QDs in a ZnSe matrix, InSb QDs in a GaSb matrix, and their predecessor InSb island on GaSb.

Closely related to “ordinary” self-ordering of QDs on a nm scale during Stranski-Krastanow growth seems to be self-ordering on an atomic scale that leads to agglomerates with internal compositional modulations. We will show that some of such CdSe and InSb rich agglomerates are in the size range of typical 3D QDs and may, therefore, constitute a new type of QDs with novel optical properties which might be exploited in further generations of opto-electronic devices.

EXPERIMENTAL DETAILS
All II-VI compound semiconductor samples of this study were grown by means of molecular beam epitaxy (MBE) at the University of Notre Dame on (001) ZnSe/GaAs pseudo-substrates [4]. The deposition of the CdSe layers that ordered themselves into QD arrangements took place at 350 °C and was
followed by the deposition of 50 nm ZnSe capping layers. Two samples were grown for comparison purposes under otherwise identical growth conditions except for the deposition of a fractional monolayer (ML) of MnSe immediately before the deposition of 2.6 MLs (0.79 nm) CdSe commenced. Only the Mn shutter was opened for a predefined time during this process, which we will term Mn “sprinkling”. Since MBE proceeds in an excess of the column VI element, effectively a fractional ML of MnSe must have been deposited, covering ideally less than 10% of the free ZnSe surface evenly. Rather slow growth rates of 0.071 ML s⁻¹ were applied for these two CdSe QDs in ZnSe matrix samples.

For a third II-VI compound semiconductor sample, 8 sequences of 10 ML (2.83 nm) of Zn₀.₉Mn₀.₁Se cladding layer (deposition rate 1ML s⁻¹) and 0.3 ML CdSe sheet (deposition rate 0.038 ML s⁻¹) were deposited at 350 °C. As the final (9th) cladding layer of the multilayer structure, 10 ML of Zn₀.₉Mn₀.₁Se were deposited and eventually a ZnSe capping layer of 50 nm was grown. Within the multilayer structure, there are, thus, nominally 87.3% of the cation sites occupied by Zn, 9.7% by Mn and 3% by Cd and we will dub it a Cd₀.₀₃Mn₀.₀₉₇Zn₀.₈₇₃Se multilayer. More details on the growth conditions of all three samples will be given in ref. [4].

All III-V compound semiconductor samples of this study were grown by metal organic vapor phase epitaxy (MOVPE) at the Department of Physics, Clarendon Laboratory of Oxford University on (001) GaSb, InAs or GaSb/GaAs pseudo-substrates [5-7]. The susceptor temperatures of the MOVPE reactor during the deposition of the InSb layers that order themselves into QD arrangements were 490 ± 10 °C. GaSb or InAs capping layers of typically 100 to 500 nm thickness were grown to cover these InSb QDs. Two sets of growth conditions were employed for the InSb QDs in GaSb matrix samples, below referred to as initial and modified growth conditions, the latter being characterized by lower III/V ratios and growth rates (approximately 1 ML s⁻¹). More details on both sets of growth conditions are given elsewhere [5-6]. Details on the growth conditions of InSb QDs in InAs matrix are given in ref. [7].

These II-VI and III-V compound semiconductor samples were analyzed by a variety of TEM modes using equipment at the University of Illinois at Chicago (JEOL JEM 2010F Schottky field emission STEM/TEM with annular dark field detector and up to 0.14 nm point resolution in Z-contrast images at 200kV acceleration voltage, JEOL JEM 3010 TEM with point resolution of approximately 0.17 nm at Scherzer focus and 300 kV) and the Department of Materials of the University of Oxford (Philips CM 20 and JEOL JEM 200CX, both operating at 200 kV). While parallel-illumination TEM in the high resolution (HRTEM) mode and the diffraction contrast (CTEM) mode are sensitive to strain fields around QDs, Z-contrast imaging in a scanning transmission electron microscope (STEM) shows in a first approximation the spatial distribution of the square of the average atomic number and is fairly insensitive to strain fields. For all analyses, plan-view and <110> cross-section specimen were prepared by the standard TEM techniques of mechanical polishing, followed by chemical polishing or ion-milling to electron transparency. TEM analyses were carried out on both capped and uncapped specimen. In order to gain more representative data from sample areas of the order of magnitude 10⁻⁷ to 10⁻⁴ μm², atomic force microscopy (AFM) was performed on uncapped InSb inlands on GaSb using a Parks Scientific Instrument SEM-BD2 scanning probe microscope at an interdepartmental facility of Oxford University.

**SELF-ORDERING SCHEMES**

In the following we will give a very brief introduction to Bimberg’s, Grundmann’s, and Ledentsov’s phenomenological classification scheme of the hierarchy of lateral self-ordered arrangements of QDs and their predecessor islands [2]. We are aware that this classification scheme is only qualitative and that the boundaries between the hierarchy levels are not well defined. At present, however, there seems to be no alternative classification scheme of self-ordered arrangements of 3D islands and QDs available. The heuristic value of this scheme is founded in both its simplicity and its capacity of representing rather complex arrangements of a very large number of QDs by simple hierarchy levels.

According to ref. [2] there are four levels to the hierarchy of self-ordered arrangements: 1st - orientation order, 2nd - shape order, 3rd - size order, and finally 4th - alignment order. Any higher level of
hierarchy includes the feature(s) of the lower level(s). While the higher levels of the hierarchy are self-explanatory, the concept of orientation order needs further clarification. At the lowest level, i.e. orientation order, 3D QDs and their predecessor islands are generally arranged at random positions, but with a preference for sites that are energetically favored such as step, mesa, or void edges, etc, i.e. locations of reduced misfit strain.

At the highest level, i.e. alignment order, we distinguished earlier between one and two dimensional alignment order. This was because we observed indications of linear (i.e. one dimensional) alignment in the Sb-based material systems we investigated [6], but not two dimensional alignment as a lateral array. Ordering into a lateral array is, however, well documented in other materials systems such as InAs on GaAs and SiGe on Si, see review [2], where the number density of 3D QDs is orders of magnitude higher than in our earlier studies on Sb-based QDs [5-6].

To our knowledge, there is no comprehensive classification scheme for vertical self-ordering of QDs or quasi-2D platelets in multilayer structures available, although considerable theoretical and experimental progress has been made over recent years (review [8]). At present, vertical arrangements of QDs/quasi-2D platelets that are separated vertically by spacer/cladding layers are classified simply as correlated, anti-correlated, and uncorrelated with respect to the lateral position of the nearest QDs/quasi-2D platelets in the lower sheet or sheets that has or have self-assembled earlier in the growth cycle.

RESULTS AND DISCUSSIONS

Enhanced lateral self-ordering in 3D CdSe QDs as a result of Mn “sprinkling”

Figure 1 shows histograms of the convolution of the shape and size distribution of 3D QDs of the sample that had a fractional ML of MnSe deposited before the deposition of CdSe commenced (Mn “sprinkling”) and a reference sample that was grown under otherwise identical growth conditions. The convolution of the shape and size distribution of the QDs was obtained by plotting the largest and smallest lateral dimension as seen in low-resolution Z-contrast STEM images, i.e. images that show negligible enlargements of the lateral dimensions of QDs as a result of surrounding strain fields. Plan-view CTEM and STEM images from both samples are shown in refs. [4] and [9]. The structural TEM observations from both samples have been correlated to a decrease of the full widths at half maximum (FWHM) of the photo-luminescence (PL) spectra from 97 meV to 50 meV as a result of the Mn “sprinkling” [4].

![Figure 1. Histograms of the convolution of the shape and size distribution of 3D QDs; 90 QDs of the Mn “sprinkled” sample (left), 78 QDs of the reference sample (right).](image)
Employing the phenomenological hierarchy of lateral self-ordered QD arrangements [2], the observations on both samples can be summarized in the statement that Mn “sprinkling” causes enhanced self-ordering of the 3D QDs. Shape and size order, i.e. the 2nd and 3rd level of the hierarchy, was achieved while the reference sample showed only orientation order. The higher hierarchy levels of the lateral arrangement of 3D QDs in the Mn “sprinkled” sample were achieved on the background of a more uniform number density (about $1.8 \pm 0.5 \times 10^{10}$ cm$^{-2}$) of the 3D QDs.

**Enhanced lateral self-ordering in InSb QDs in GaSb matrix and their predecessor islands as a result of lower $\text{III}/\text{V}$ ratios and growth rates**

AFM examinations on uncapped InSb on GaSb samples grown under the initial growth conditions revealed the co-existence of three different types of three-dimensional InSb islands on GaSb [6,10,11]. Orientation order, i.e. the lowest level of the phenomenological hierarchy of lateral self-ordered arrangements [2] was observed, due to preferential 3D island nucleation at step edges [11]. From the non-uniform distribution of the direction vectors of the typically occurring “black-white” contrasts with respect to the diffraction vector in CTEM, the conclusion could be drawn that there was essentially no shape order in capped and uncapped samples [5]. HRTEM on capped cross-section specimens showed later [11] that it is the varying degree of curvature of agglomerates with a shape similar to “convex lenses”, that caused these observations. The best samples of this first series possessed FWHM of the 3D QDs PL peaks as low as 15 meV [6,10].

For the modified growth conditions, i.e. lower growth rates and $\text{III}/\text{V}$ ratios, we obtained shape and size order, i.e. the 2nd and 3rd level of the lateral self-ordering hierarchy [2], but intermediate growth conditions led only to shape order [6]. The general trend observed was the lower the $\text{III}/\text{V}$ ratio and growth rate, the higher the level of self-ordering of the InSb islands and QDs. The FWHM of the 3D QD PL peaks of the best samples of this second series were as low as 10 meV [6], correlating with a better QDs shape and size distribution for the samples with lower $\text{III}/\text{V}$ ratios and growth rates.

**Vertical self-ordering of quasi-2D platelets and internal compositional modulations on the atomic scale in Cd$_{0.5}$Mn$_{0.056}$Zn$_{0.444}$Se agglomerates in Mn$_{0.1}$Zn$_{0.9}$Se matrix**

The co-existence of at least four different types of CdSe rich agglomerates in close proximity was observed in the Cd$_{0.03}$Mn$_{0.097}$Zn$_{0.873}$Se multilayer structure. The first type of these agglomerates were easily recognizable by their pronounced strain fields in cross-section HRTEM images. These agglomerates were of the lateral order of magnitude 5 nm and may be considered as quasi-2D platelets. In addition to uncorrelated vertical platelet arrangements, we observed vertically correlated as well as anti-correlated arrangements in close proximity. This part of our study is in reasonable agreement with experimental results of other authors [12] for ZnSe spacer layer thicknesses of around 3 nm and CdSe sheets of nominally the same thickness as in our study.

Besides much larger (order of magnitude 100 nm) anisotropically shaped agglomerates with internal compositional modulation on the atomic scale in Z-contrast STEM images [4,9], a rather isotropically shaped agglomerate (order of magnitude 25 nm) was observed in HRTEM to be free of structural defects, did not possess a significant strain field, but an internal compositional modulation on the atomic scale with a periodicity of approximately 0.7 nm, Figure 2. As it is of the size of typical 3D QDs, this agglomerate may be considered as a novel type of QDs. The analysis of the Fourier transform of this agglomerate indicated an ordering in successive $\pm (-111)$ planes [13]. Atomic ordering of the cations on every second crystallographic plane implies an aggregate composition of Cd$_{0.5}$Mn$_{0.056}$Zn$_{0.444}$Se, which would also be compatible with the observed periodicity in Fig. 2. If the proposed composition were correct, this novel type of QDs would contain significantly more Cd than “ordinary” QDs originating from the deposition of fractional CdSe MLs [14] and should, therefore, dominate the PL spectrum. Agglomerates with different types of internal compositional modulation on the atomic scale and with
sizes of the order of magnitude 5 - 10 nm were also observed in atomic resolution Z-contrast STEM images, e.g. Figure 3, to coexist in close proximity. Selected area electron diffraction patterns showed superstructure reflections that indicated the co-existence in close proximity of atomic arrangements [4] that have not been reported before in the literature on II-VI compound semiconductors [15].

At present, we do not know why agglomerates with different types of self-ordered atomic arrangements and varying sizes have formed in addition to the multi-sheet quasi-2D platelets that were expected to grow. If the ongoing self-ordering processes were, however, of a dissipative nature [3], the co-existence of agglomerates with different atomic arrangements, i.e. differences in configurational entropy, strain status, and size could be a quite common phenomenon.

**Internal compositional modulations on the atomic scale in InSb rich agglomerates in InAs matrix**

Internal self-ordered compositional modulation with a similar phenomenology as mentioned above were also observed by atomic resolution Z-contrast imaging and HRTEM in single-sheet 3D InSb QDs in an InAs matrix. Again these agglomerates may be tentatively considered as constituting a novel type of 3D QDs which is distinguished form “ordinary” 3D QDs by its internal atomic scale compositional modulation. Samples from this series showed PL peaks at approximately 3.5 and 4 μm wavelength with FWHM of 26 - 30 meV [5,7]. The origin of these PL peaks remained controversial and these peaks may be due to “ordinary” [7] and/or novel QDs.

The observation of internal compositional modulations on the atomic scale in a second QDs system and a single sheet arrangement suggests that self-ordering at the atomic scale may be a more widespread phenomenon in self-assembled QDs that are grown in the Stranski-Krastanow mode.

**CONCLUSIONS**

The phenomenological hierarchy of laterally self-ordered arrangements of 3D QDs was successfully applied to CdSe QDs in ZnSe matrices, InSb QDs in GaSb matrices, and their predecessor InSb islands on
GaSb. Higher hierarchy levels of self-ordering and better optical properties were achieved in both QDs systems by modifications to the growth conditions, demonstrating the heuristic value of the employed phenomenological model. Vertically correlated, anti-correlated, and uncorrelated self-ordered, quasi-2D platelets coexist in a $\text{Cd}_{0.03}\text{Mn}_{0.097}\text{Zn}_{0.873}\text{Se}$ multilayer structure in close proximity to CdSe rich agglomerates with various types of self-ordered internal compositional modulation on the atomic scale. The coexistence of differently strained and sized agglomerates with differences in the configurational entropy in close proximity as well as the phenomenon of atomic self-ordering in representatives of both II-VI and III-V compound semiconductors which were grown by different techniques suggests that self-ordering of both single-sheet and multi-sheet QD arrangements may be of a dissipative nature.

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REFERENCES

3. Self-ordering processes can be either conservative or dissipative. An example for conservative self-ordering is the formation of crystalline structures with low energy content at moderately low temperatures close to thermodynamic equilibrium. Dissipative self-ordering, on the other hand, is a process that takes place far from thermodynamic equilibrium and is the subject of a relatively young branch of theoretical physics that is called synergetics. For a textbook on the subject see: H. Haken, Synergetics, An Introduction, Nonequilibrium Phase Transitions and Self-organization in Physics, Chemistry and Biology, (Springer-Verlag Berlin, Heidelberg, New York, 1978).
13. The also present $\pm \frac{1}{2}$ (-113) extra spots were probably due to double diffraction effects.