# Self-Assembly and Self-Organization of Semiconductor Nanostructures

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**Abstract**

This paper reviews the present status of self-processes for semiconductor nanostrutures. The term "self-process" includes the concepts of self-assembly and self-organization, which is clearly distinguished following Lehn's definition. We describe self-assembled InAs islands grown on a GaAs (100) surface and self-organized InGaAs disks grown on a GaAs (311)B surface. We touch on the future aspects of a novel role for nanostructures via semiconductor self-processes.

## 1. Introduction

Fabrication techniques for semiconductor nanostructures, such as quantum dots and quantum wires, are principally based on a combination of quantum well growth and lateral fine lithography. However, mechanical damage to the interfaces in the etching process is becoming a serious problem in sub-100nm-sizes [1]. In order to overcome this problem, recently, much attention has been focused on self-processes in epitaxial growth in fabricating damage-free nanostructures. Here, the term "self-process" includes primarily the concepts of self-assembly, self-organization, and replication, whose terminology was proposed by J.-M. Lehen in the field of Supramolecular Chemistry [2, 3, 4]. Here, one can consider that cluster formation in the crystal growth is one of the self-processes via adatom motion in the chemistry field. The term of self-assembly has a broader meaning. In particular, a Stranski-Krastanov (S-K) mode grown InAs island [5] under study again during the last few years, was called a "self-assembled dot" because it spontaneously emerged and assembled a three-dimensional nano-scale structure with a random distribution [6,7]. However, the full-width at half-maximum (FWHM) of photoluminescence from large ensembles of dots is still broader than that of quantum wells, while a series of ultra-narrow lines due to emission from single dots has been reported at low temperature [8]. Other self-assembling processes in crystal growth for semiconductor nanostructures may be seen in selective epitaxy [9] and droplet epitaxy [10], while they will not be discussed here.

In 1993, however, we found, in a strained InGaAs/AlGaAs system on a GaAs (311)B substrate during metalorganic-vapor-phase-epitaxial growth, a novel phenomenon leading to the formation of well-defined, well-ordered arrays of nanocrystals with built-in InGaAs strained quantum disks having diameters between 150-30 nm. We call this confined nanostructure a "self-organized disk", because it is associated with pronounced ordering [11,12]. This surface rearrangement process resulting in the stationary pattern formation of the various quasi-periodic nanostructures seems to belong to the class of a Turing-type self-organization phenomenon of synergetic in non-linear dynamic systems [13-16]. The most important discovery was that the built-in InGaAs quantum disks, within the nanocrystals, exhibit a strong, narrow-line photoluminescence (PL) emission even at room temperature, when compared with the reference quantum wells grown side-by-side on the (100) surface. The well-resolved exciton resonances in photo-luminescence- excitation (PLE) spectra indicate the structural perfection and efficient localization of excitons in our quantum disks [12]. This indicates that self-organization might produce nanostructures of the quality needed for devices [17].

In this paper, we will review the present status of the self-processes for semiconductor nano-structures, emphasizing self-organized disks on a GaAs (311)B surface in comparison with self-assembled islands on a (100) surface.

## 2. Self-assembled islands

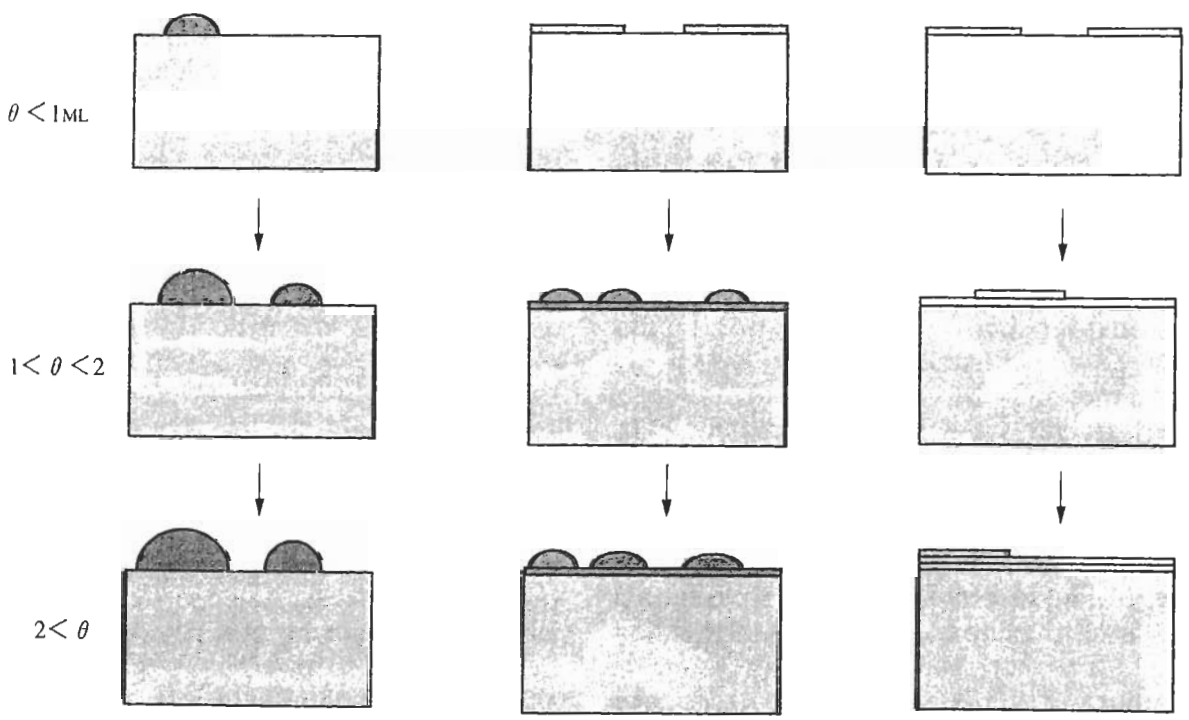
*Classifiction*

On the basis of equilibrium thermodynamics, there are three basic modes for crystal growth in the absence of surface defects and interdiffusions as shown in Figure 1 [18]: these are Volmer-Weber (V-M: 1926), Stranski-Krastanov (S-K: 1939), and Frank-van der Merve (F-M: 1949). These may be described as island growth, layer-by-layer plus island growth, and layer-by-layer growth. The growth mode that the system adopts depends crucially on the surface free energy of the material, the interfacial free energy, and the lattice mismatch between the atoms in the film and the substrate. In the field of thin semiconductor crystal growth, molecular-beam-epitaxy (MBE) and metal-organic vapor-phase-epitaxy (MOVPE) have been developed to precisely fabricate thin quantum well structures on an atomic scale. A standard F-M homoepitaxial growth in vapor phase epitaxy is based on a so-called step-flow BCF (Burnston-Cabrera-Frank) model, which is basically described by the simple diffusion partial differential equation, in which the density c of adatoms obeys the mass conservation law [19].

*Self-assembly in island formation*

In particular, for systems with low interfacial energy and a large lattice mismatch, the initial growth takes place in a layer-by-layer fashion (a so-called "wetting-layer"). However, as the film thickness increases over the critical thickness, the strain energy continues to build up, and the system can eventually lower its free energy by forming a three dimensional island in which the strain is relieved by misfit dislocation. This spontaneous formation of three-dimensional islands is described as an S-K self-assembling process without any ordering. While no complete model is yet available, the phenomenological nucleation approach was developed by Venables using a rate equation method: The primary dynamical variables are the areal densities of adatoms, n1 and subcritical and stable clusters, denoted by nj and nx [20].

Fortunately, for the typical InAs/GaAs (6.5% mismatch) hetero-semiconductor system, the diameter and the height of these




(a) V-W mode (b) S-K mode (self-assembly) (c) F-M mode

**Fig.1** Clasification of the three possible growth modes, based on equilibrium thermodynamics: Volmer-Weber, Stranski-Krastinov, and Frank-van der Merwe. $\theta$ represents the coverrage in monolayers (ML).

self-assembled islands for a InAs coverage of 1.75ML is estimated as around 20-30 nm and 6nm in the nanometer range, respectively [6]. An increase in island areal density with a random distribution becomes saturated with a small increase InAs coverage, resulting in the irregularity in size. The size uniformity was ± 10% in height and ± 7% in diameter only in the initial stages of the S-K mode transition. The typical PL emission from InAs S-K islands with a diameter of 30nm is located around 1.1-1.3 eV with a 60 meV broad FWHM typically at 10 K. [5, 7]

Lateral alignment of InAs islands has been observed due to the preferential nucleation at step edges [6]. More directly, with actual control over the position of the islands, the S-K mode on prepatterned susbtrates has been studied to selectively place InAs islands in chains along trenches or in small numbers in arrays of holes formed on patterned GaAs (100) substrates [21]. The vertical alignment of S-K islands with thin spacer layers has been observed and is attributed to the non-uniform strain fields during overgrowth [5].

The detailed optical properties of buried S-K InAs islands have been examined with micro-PL spectroscopy. Observed splitting of the PL spectra into a series of ultranarrow lines with linewidths less than 0.15 meV is attributed to the zero-dimensional localization of excitons in InAs islands [8]. In addition, laser operation with quite a high threshold current of below 100K has been reported for a single stack of InGaAs islands in the active region [22].

## 3. Self-organized disks

*Turing instability*

Crystal growth of thin films from atoms deposited from the gas phase is intrinsically a nonequilibrium phenomenon. In general, nature exhibits a number of dissipative structures in the system kept far from equilibrium by permanent driving forces. Nonlinear dissipative mechanisms have been proposed as providing a possible underlying process for some aspects of biological self-organization, pattern formation, and morphogenesis [13-16]. In particular, Turing structures [13] are typical stationary periodical concentration patterns resulting from a diffusive instability originating from the sole coupling of reaction and diffusion processes in nonlinear dynamical systems. They correspond to stable stationary solutions of a set of reaction-diffusion equations composed of nonlinear partial differential equations based on the two-species model. Although predicted by

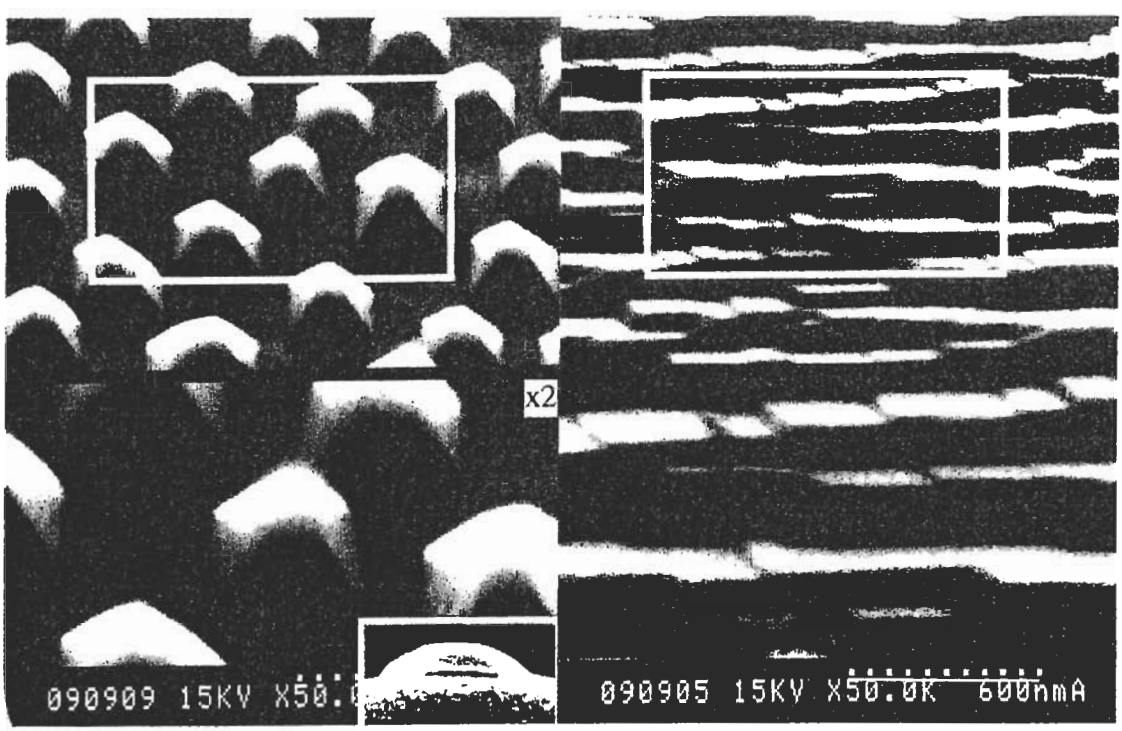



**Fig.2** SEM images of as-grown 10-nm-thick $In_{0.2}Ga_{0.8}As$/AlGaAs on (a) GaAs (311)B, and (b) GaAs (311)A . The SEM cleaved cross-section is also shown with an inset of the magnified view of the (311)B sample. The substrate temperature was as high as 800°C during the growth.

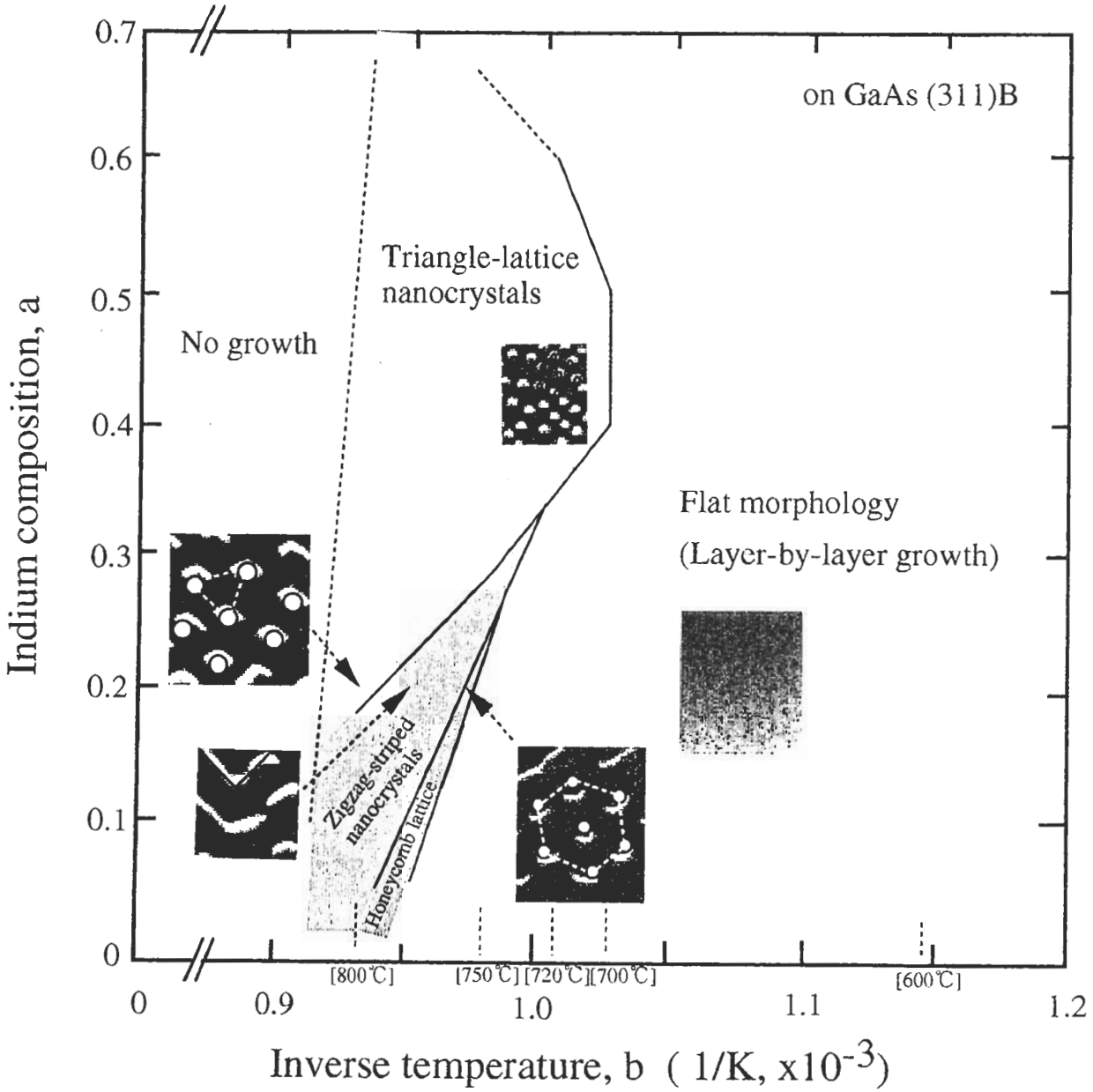



**Fig.3** Surface topography domain of as-grown InGaAs on the GaAs (311)B as functions of the indium composition and the inverse substrate temperature.

Turing in 1952, clear evidence was not obtained until recently. In 1990, De Kepper and colleagues observed the first experimental evidence for Turing structures in a chemical system, the chlorite-iodide-malonic acid (CIMA) reaction [23].

*Self-organization in disk formation*

Here we introduce the Turing-type self-orga-nizing process on the high-index GaAs (311) surfaces. The samples were grown in a vertical low-pressure MOVPE reactor using rf heating. Typical SEM topographical images of as-grown, 10-nm thick $In_{0.2}Ga_{0.8}As$/ AlGaAs on GaAs (311)B and (311)A surfaces are shown in Fig. 2 [24] . While we got a flat homo-geneous pattern of InGaAs on a GaAs (100) surface, we found well-defined, well-ordered arrays of nanocrystals in a triangular lattice and periodically-corrugated surface on (311)B and (311)A surfaces, respectively. As discussed in detail in Reference 11, these nanocrystals contain the built-in InGaAs quantum disks. Figure 3 roughly summarizes a surface morphologies domain as a function of indium content and inverse temperature of the substrate. The central region indicates completely-isolated nanocrystals with different sizes. Basically, the disk size of the triangle-lattice nanocrystals in diameter can be roughly controlled in the range of 150 nm to 60 nm by changing the indium composition. The

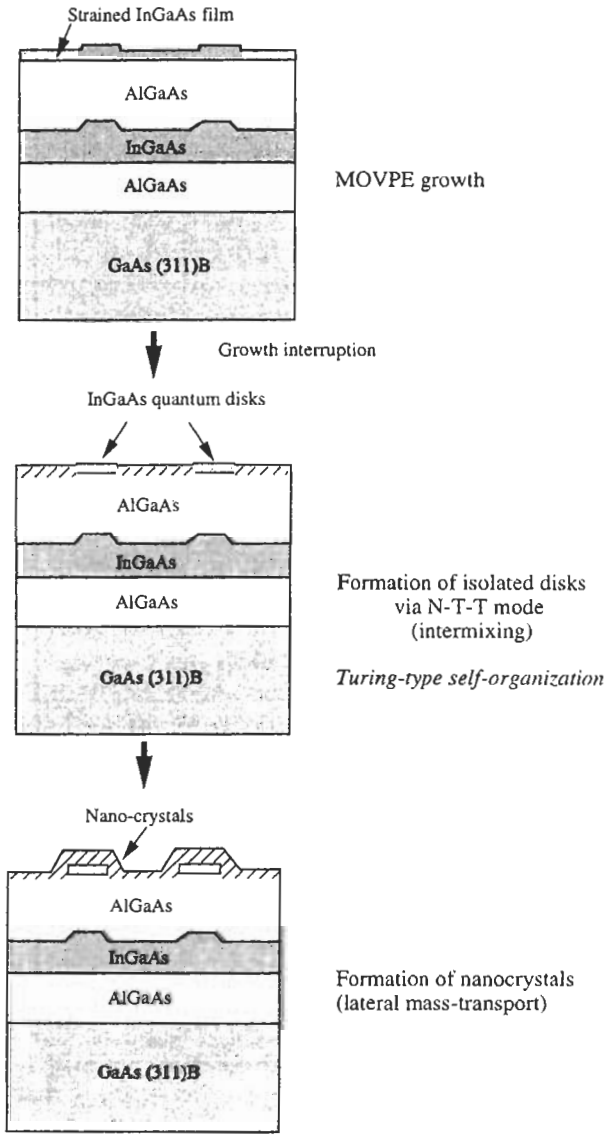



**Fig.4** Schematic view of the surface rearrangement process of InGaAs/AlGaAs on GaAs (311)B. The novel growth mode of self-organization on high-index planes was discovered by Nötzel, Temmyo and Tamamura (N-T-T) in 1993.

estimated wavelength, (i. e., the period of the neighboring nanocrystals) is between 450 and 130 nm, while the areal density changes somewhat with changes in the nominal InGaAs thickness. We also found various periodical patterns such as complex, modulated surface patterns, including a honeycomb lattice, a reciprocal triangle lattice, and a zigzag-striped nanocrystal pattern. The honeycomb lattice was very crucial. For a (311)A surface, we also got a different surface morphology domain for a similar strained system, which consists of corrugated and triangle-lattice patterns. Here, as-grown lattice-matched GaAs/AlGaAs on the (311)A surface also revealed a corrugated morphology [25].

The mechanism of the rearrangement process on the GaAs (311)B faces is illustrated in Figure 4. The phenomenological explanation is as follows. During growth interruption, the nearly flat InGaAs film redistributes itself into isolated disks as a result of the physical reaction of intermixing with underlying AlGaAs. The isolated disks are then buried by intermixed AlGaAs due to lateral mass-transport, resulting in the formation of well-defined and well-ordered arrays of nanocrystals with low-index crystal facets under a relatively high substrate temperature. The mechanism of this rearrangement seems to be quite different from that of the conventional S-K growth mode of the simple self-assembled islanding phenomenon.

If one would like to try the phenomenon using the non-linear reaction-diffusion mechanism via Turing instability, the existence of the large difference in the diffusion constant of at least two species is needed in the model. The two diffusible species on the (311) surfaces in the strained semiconductor heterostructure system are not clear at present, in contrast to the CIMA chemical reaction system. However, these results may be due to unique features of the GaAs (311) surfaces. For the (311)B case, there exist two kinds of sites on the surface: the double dangling bond site seen in the [100] direction, and the single dangling bond site seen in the [111]B direction. Their densities are exactly the same. In addition, there are no atomic steps along the [011]. Because of the arsenic-stabilized surface due to the single dangling-bond of arsenic, it is very difficult to grow epitaxial layers, such as GaAs and AlGaAs films, on the GaAs (111)B substrate [26]. Note, that the formation process on the (311)B face is somewhat related to the difference of the adsorption rates on the (100) and (111)B faces. Accordingly, our physical rearrangement process seems to involve antagonistic activatory and inhibitory kinetic processes induced by the (100) and (111)B faces. The intermixing process seems to correspond to the reaction process in the chemistry. We can translate the chemical term "reaction-diffusion system of the molecules" to the crystal growth term "intermixing-diffusion system of the adatoms." In particular, a species controlling the inhibitory process

must diffuse faster than a species controlling the activatory process. However, the actual diffusion constants for the two species are not known, which indicates that more detailed analysis will be needed.

Here, we provide additional notification that the as-grown surface morphology of almost lattice-matched GaAs/AlGaAs reveals a flat morphology on a (311)B surface. Although lateral mass transport does not take place (see Figure 4), we do not think this flat surface means that self-organization cannot occur just under the (311)B surface. We do not have any clear evidence yet, but are continuing our investigation.

We will briefly touch on the case of the (311)A surface. Usually, the microsteps formed on the crystal surface described as the result of "step-bunching", as in the case of the vicinal surface growth of a low-index surface such as a (100) surface. However, this scheme does not seem to correspond to that of the (311)A case because the alignment direction of the periodic corrugation on the (311)A face is almost perpendicular to that of the intrinsic atomic microsteps of the (311)A. We believe that a similar nonlinear reaction-diffusion mechanism, including activatory and inhibitory processes, covers the rearrangement process on the (311)A surface, which may be caused by the difference in adsorption rates of the (100) and (111)A sites.

Here, we will describe some additional features of the self-organized disks. We successfully applied this phenomenon to build novel $In_{0.25}Ga_{0.75}As$ quantum disk lasers with a low-threshold and a power-saturation tendency at room temperature [17]. When we increased the indium content up to 40% to produce smaller InGaAs disks with a nominal thickness of 3 nm and a size of around 30 nm, the linewidth of the PL emission became wider at room temperature, up to a FWHM of over 30 meV [12]. This may have been caused by the influence of the relative fluctuation in the thin film thickness associated with the high indium content. We observed very sharp luminescent lines (<0.1meV) from these smaller disks (clusters) with micro-PL/PL-excitation spectroscopies at 10 K, which suggests a zero-dimensional subband structure [27, 28]. Moreover, we have recently shown the possibility of site control using the novel technique of a resonant self-organization composed of selective epitaxy and a Turing-type self-organization phenomenon on a (311)B surface [30].

The unique surface morphologies on GaAs (311) surfaces suggest a novel growth mode due to Turing-type self-organization in addition to conventional growth modes. We have also found that this self-organization process also occurs on InP (311) substrates [31], and may be common to III-V compound semiconductors. We have confirmed the unique features on other high-Miller-index GaAs surfaces, suggesting that Turing-type self-organization possibly dominates the epitaxial process under high temperature growth conditions besides the growth on the vicinal surface of low-index surfaces such as (100), (111)A/B and (011). This may be emergence of *the complexity*.

## 4. Summarizing remarks

Research on low-dimensional nanostructures has been renewed by the introduction of self-processes in semiconductor crystal growth. However, an advanced damage-free nanofabrication technique with a higher controllability and, simultaneously, a device concept for nanostructures of which the characteristics are size-fluctuation free will be needed in the near future.

A novel approach to semiconductor nano-structure encountered research also seems to be emerging: Playing a pioneering role in the active regions of novel optical devices composed of new exotic material systems, even with a large lattice-mismatch.

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1. Recent progress on ultra-low threshold vertical-cavity surface-emitting lasers, large To 1.3μm GaInNAs laser diodes (LDs), and high speed strained quantum well LDs, have shown important improvements in semiconductor LDs with practical wavelength-windows. Therefore, it seems that the idea of replacing conventional quantum well active regions with low-dimensional nanostructures to achieve a lower threshold, larger To, and higher speed operation has become less

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