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Complex Nanostructures by Pulsed Droplet Epitaxy

Invited Feature Article

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Abstract What makes three dimensional semiconductor quantum nanostructures so attractive is the possibility to tune their electronic properties by careful design of their size and composition. These parameters set the confinement potential of electrons and holes, thus determining the electronic and optical properties of the nanostructure. An often overlooked parameter, which has an even more relevant effect on the electronic properties of the nanostructure, is shape. Gaining a strong control over the electronic properties via shape tuning is the key to access subtle electronic design possibilities. The Pulsed Dropled Epitaxy is an innovative growth method for the fabrication of quantum nanostructures with highly designable shapes and complex morphologies. With Pulsed Dropled Epitaxy it is possible to combine different nanostructures, namely quantum dots, quantum rings and quantum disks, with tunable sizes and densities, into a single multi-function nanostructure, thus allowing an unprecedented control over electronic properties.

Keywords Quantum Nanostructures, III-V semiconductors, Droplet Epitaxy

1. Introduction

The principle of nanotechnology is the manipulation of the matter at the nanoscale in order to take advantage of the different physical properties of materials via size and shape fine tuning. Amongst the more relevant nanoscience advancements an important place is taken by quantum confinement effects that take place in three dimensional semiconductor nanostructures. Because of them, these quantum nanostructures (QN) can be considered as artificial atoms and like the natural atoms show a discrete spectrum of energy levels [1]. More than natural atoms, QNs electronic properties can be finely tuned, on demand, adjusting structural parameters, such as size, composition and morphology. The latter parameter is the most relevant for the control of the QN electronic properties, as tiny variations in morphology can cause dramatic changes on the electronic properties [2]. One of the most pursued method for the fabrication of QNs is the molecular beam epitaxy (MBE) growth of lattice-mismatched III-V semiconductor materials via the Stranki-Krastanov (SK) mode [3]. This technique exploits

the self-assembly of pyramidal-like QNs, driven by the relaxation of strain accumulated in the epilayer. Despite the high success of the technique, which led to fundamental physical understandings and to a variety of applications [3-5], the available design degrees of freedom remain limited. The precise engineering of size and shape of QNs via SK self-assembly remains problematic [6], thus limiting the possibilities of a real on demand design of the electronic properties. It is worth

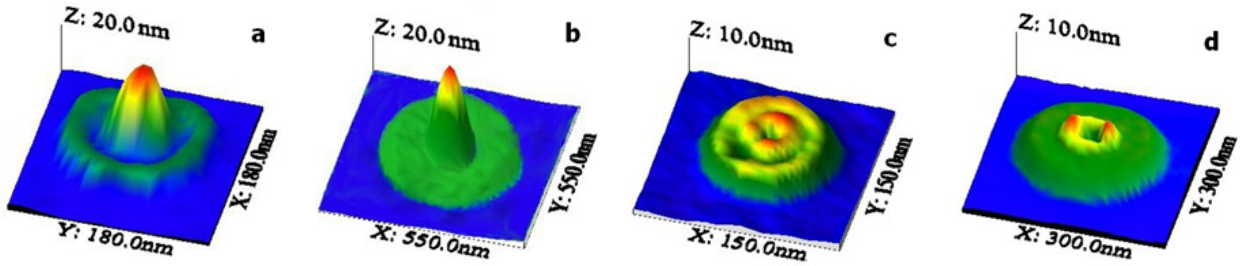

Figure 1. Atomic force microscope (AFM) images of dot/ring (a), dot/disk (b), ring/ring (c) and ring/disk (d) GaAs/AlGaAs QNs

mentioning that the possibility to control QN shape allows to access fundamental quantum design parameters that include geometrical quantum phase [7], spin-spin interaction [8] and quantum state couplings [9].

2. The Pulsed Droplet Epitaxy

To overcome the SK growth limitations, a kinetic limited growth procedure, the Pulsed Droplet Epitaxy (PDE), a variant of molecular beam epitaxy (MBE), was introduced [10–14]. Unlike the SK self-assembly technique, PDE does not rely on strain for the formation of three-dimensional (3D) crystals. PDE is based on the pulsed deposition of III and V column elements at controlled temperatures and fluxes. In this respect, PDE can be considered as a variant of the well established droplet epitaxy growth technique [15,16], which demonstrated the possibility to grow QNs with shapes ranging from dots [17] to rings [10,18]. The first step of PDE is the formation, in an MBE environment, of nanoscale reservoirs of metal atoms on the growth surface in forms of nanometer size droplets with small size dispersion. This is achieved in a group V free environment. The metallic droplet on the surface will constitute the group III localized sources from which the QNs will evolve. Second, and more relevant for the QN shape control, is the pulsed supply of group V elements at different temperatures and fluxes, for the transformation of the metallic droplet into the QN. The possibility to finely control, through flux and temperature, the transformation kinetics of the metal droplets in to III-V nanocrystals allows for the formation of QNs with complex and controlled shapes. In particular it is possible to combine quantum dots, rings and disks in a single, multi-function QN. We show here (Fig. 1) some examples of complex GaAs QNs grown on $Al_{0.3}Ga_{0.7}As$ buffer layers. The presented QNs are made by a dot or a ring at the center and an outer region made by a ring or a disk. The fabrication of the reported composite QNs is made in a multiple step procedure which include first the Ga droplet deposition and then several As supply steps at different temperatures and fluxes, as detailed in Refs. [10,13,14,18]. Let us follow in more detail the PDE fabrication. When Ga is deposited on AlGaAs (100) group III terminated surface (4x6 reconstruction [19]), it self-assemble in form of small droplets, whose size and density can be finely tuned by substrate temperature, Ga flux and coverage. When droplets with the required density and size are formed, PDE fabrication of QNs proceeds via the supply of predetermined As quantities at controlled fluxes and substrate temperatures. This allows for the fine control of the three phenomena that are occurring during the As supply: i) the thermodynamically driven diffusion of Ga atoms from the droplets to form a two dimensional (2D) layer on the substrate; ii) The incorporation of As in the liquid Ga at the droplet original position, thus developing a 3D nanocrystal; and iii) the kinetic of the change in the surface reconstruction around the droplets from Ga-rich to As-rich, caused by the adsorption of As on the flat surface. The interplay between these phenomena sets the final configuration of the GaAs nanostructure, between the limit cases of a total lateral growth of GaAs around the droplet edges (strong Ga diffusion) and of a complete crystallization of Ga within the original droplets (very efficient As incorporation). It is possible to switch between the 2D (ring and disk shapes) and 3D (dot shapes) growth modes and set Ga diffusion pinning sites by changing the As flux and substrate temperature conditions during the PDE fabrication process. Indeed a strong diffusion of Ga is found at lower As flux and/or higher temperatures and therefore under these conditions the lateral 2D growth will be predominant (ring and disk); for higher As flux and lower substrate temperatures, instead, the development of a 3D structure is favored (dots). Finally the change in the surface reconstruction which appears due to the As adsorption on to the substrate surface during the crystallization can be used to finely tune the shape of the laterally grown GaAs between a flat disk and a ring [12]. As rule of thumb, disks are obtained at temperatures above 350 °C, while lower temperatures give rise to ring shapes. In both cases, As pressure is maintained in the 10^{-6}-10^{-7} Torr range [12]. Dots require low growth temperatures (below 200 °C) and high As fluxes (higher than 10^{-5} Torr) [17]. PDE allows to switch between different growth modes during a single QN fabrication, thus achieving complex, composite, structures. This is the key factor introduced by PDE growth protocol, that is multiple crystallization steps, performed at different temperatures. With short time As pulses (on the order of seconds) we can

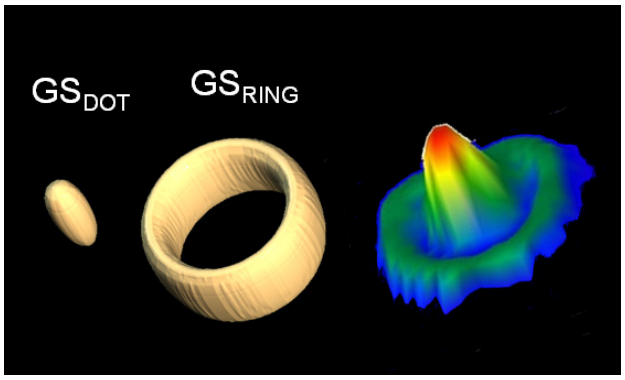

Figure 2. Isosurface plots of the electronic probability density at 50% of the maxima in the dot/ring. From left to right, these panels show the wave function of the ground state of the nanostructure, which corresponds to a wavefunction totally localized in the dot, and that of the an excited radial state, fully localized in the ring. The AFM profile of a dot/ring structure is reported as well.

selectively crystallize only a fraction of the Ga atoms stored in the droplets reservoir on the surface and subsequently change the conditions for next step, thus combining different building blocks within a single QN. The PDE nanostructures electronic and emission properties were extensively studied showing high optical quality [20], peculiar carrier dynamics [21] and single photon emitter properties [22].

The introduction of the high shape flexibility in the QN design, allowed by PDE, leads to a deep change in the way nanostructure based devices are devised. For the first time it is possible to fabricate QNs where the electronic properties are designed on demand for a specific device function via shape engineering, that is the *form follows function approach*. PDE allows for the fabrication of QNs where optical properties, intersublevel energy spacing, level dimensionality and even the interaction between nearby QNs are freely accessible for engineering. In fact, the change in shape of a QN often leads to a change in electronic state symmetries and characteristics, thus the relevant phenomena are much richer. At its basic level, the change in electronic structure is the change in single-particle electronic states. This includes the state energy, the overall shape of the wave function, the symmetry, the polarization, and the localization. In order to gain better insight on the effective ability of our QNs to effectively tune single-particle electronic states we performed theoretical calculations based on effective mass approximation [20]. The results for a typical dot/ring QN are reported in Fig. 2. Both dot and ring are capable of quantum confinement, giving rise to the well know ladder of quantum states belonging to carriers confined in the dot and the ring. More details on the electronic states and the comparison with the observed photoluminescence emission can be found in Ref. [14]. Many-body interaction should be strongly influenced as well. The shape design possibilities introduced by PDE permit to fabricate complex QN made by quantum units of different geometry and dimensionality. This permits to finely tune the electronic property of the QN and, more relevant to applications, the QN response to external fields. In fact, the coupling between states belonging to different parts of the QN can be switched on or off due to selection rule breaking due to external fields [9]. Recent theoretical investigations indicated that changes in QN shape are accompanied by an alteration of the ground state total spin [8,23], thus making possible to devise tunneling spin switches. In addition, the dimensionality of the QN, namely zero, one or two dimensions, plays a fundamental role, changing the way the QN responds to external fields. Infrared detectors made by quantum dot embedded in a quantum well show increased performances, due to better coupling between zero dimensional dot and two dimensional well electronic states respect to bulk states. Via PDE we can devise single QN dot in a well photodetector where dot and well are both included in a single QN. As a further demonstration of the potential of PDE approach we fabricated even more complex systems, as shown in Fig. 3. Again the multi-step synthesis was applied, selectively forming each block of the QN at different temperatures. Here two As shots at low pressure and relatively high temperature (thus in the 2D growth mode conditions) were applied to the Ga droplet ensemble to obtain the ring/ring/ring sample [10]. The dot/ring/ring required as well two As shots in 2D growth mode followed by a low temperature and high As flux. The latter is needed to freeze the metallic Ga which remains in the central part of the nanostructure after the two initial As shots, into the central dot [14].

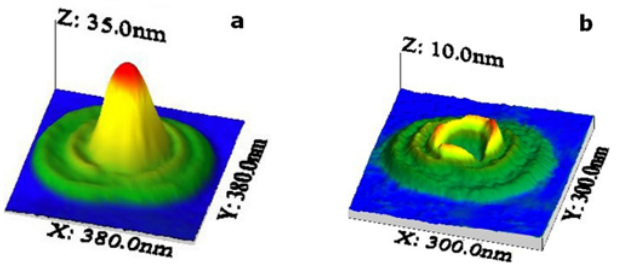

Figure 3. Atomic force microscope images of dot/ring/ring (a), ring/ring/ring (b) GaAs/AlGaAs QNs.

3. Conclusions

In conclusion, with PDE, it is possible to grow semiconductor coupled quantum systems, fabricated with a pure self-assembly technique, based on multiple, partial crystallization steps of the Ga. PDE allows for the realization of complex QNs where single building blocks, such as quantum dot and rings, can be combined together with a high shape flexibility. PDE can be therefore used as basis for the conception of novel devices in optoelectronics and quantum information fields, as well as for the investigation of phenomena in fundamental physics.

4. Acknowledgments

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5. References

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