

12-1-2004

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Suggested Citation

Liang, Jianyu , Luo, Hailin , Beresford, Rod , Xu, Jimmy (2004). A Growth Pathway for Highly Ordered Quantum Dot Arrays. *Applied Physics Letters*, 85(24), 5974-5976.

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A growth pathway for highly ordered quantum dot arrays

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(Received 7 July 2004; accepted 25 October 2004)

To realize the desired zero-dimensional behavior of a quantum dot ensemble, the ability to fabricate quantum dots with a high packing density and a high degree of size, shape, and spacing uniformity is crucial. Here we report highly ordered InAs nanodot arrays grown by molecular-beam epitaxy on nonlithographically nanopatterned GaAs. Approximately 20 billion dots are grown in a 1 cm² area with the smallest size dispersion ever reported and forming a lateral superlattice in hexagonal dense packing form. These techniques presage a pathway to controlled growth of periodic quantum dot superstructures, which offer macroscopic spatial coherence in the interaction of quantum dots with radiation. © 2004 American Institute of Physics. [DOI: 10.1063/1.1834987]

As an artificial atom, the semiconductor quantum dot (QD) is attracting intensive research attention, which aims to untangle the subtle interplay of crystal morphology (size, shape, strain, and cladding) with the quantum dynamics of the interaction with the optical field. Tremendous efforts over many years have led to phenomenal successes in growing QDs by self-assembly mechanisms based on the precision control and delicate balance of the strain-mismatch conditions. These advances have enabled the development of a new generation of electronic and optoelectronic devices as well as empowered the studies of biomolecular systems and fundamentally interesting quantum phenomena.¹⁻⁵ What has been lacking to date, however, is an effective means to synthesize three-dimensional (3D) confined nanostructures which also possess a high degree of spatial ordering, that is, uniformity not just of size and shape, but also of the spatial relationship between the dots. What is ideally desired is a periodic superstructure of uniform QDs. For many applications, it is also desirable to have the QDs in a densely packed form. Moreover, QD growth by self-assembly, while being successful, has been constrained to a few material compositions and size ranges in which the critical strain-mismatch conditions can be met, and it would be desirable to have a greater range of choices in QD composition and sizes. These goals, however desirable, are unlikely to be attainable in the present self-assembling growth regime because of the absence of a feedback mechanism that would allow the self-assembled QDs to self-organize into a highly ordered array. We are thus compelled to explore alternative pathways to QD synthesis.

We found that it is possible to direct and confine the growth of InAs QDs on a nanocavity array that is imprinted into the GaAs substrate surface via a highly ordered nanopore array template which is itself formed and self-organized in an anodic aluminum oxide (AAO) membrane. Scanning electron micrograph (SEM) images of the resulting densely packed two-dimensional (2D) periodic dot arrays vividly reveal an unprecedented high degree of ordering and uniformity together with hexagonal dense packing [Figs. 1(a) and 1(b)]. The internal atomic structure of the QD proves to be just as good, as confirmed via x-ray diffraction (XRD) and

high-resolution transmission electron microscopy (TEM). The techniques employed here presage a pathway to controlled growth of periodic quantum dot superstructures, which offer the new element of macroscopic spatial coherence in the interaction of QDs with radiation.

Our directed-growth method, illustrated in Fig. 1, combines a nonlithographic pattern transfer (that can be scaled to large areas) with selective nucleation of Stranski-Krastanov (SK) islands, thus combining high dot density, high crystal quality, size uniformity, and spatial periodicity. Approximately 20 billion dots are grown in a 1 cm² area with a size dispersion less than 10% and a significant degree of long-range positional and orientational order, forming a lateral superlattice in hexagonal dense packing form.

To enable directed growth the GaAs substrate is patterned by reactive ion etching (RIE) using an AAO membrane as the mask. Nanopore arrays formed during anodization of aluminum have been observed and reported since the 1950's.^{6,7} More recently, hexagonally ordered nanopore arrays with periodicities from 50 to 420 nm have been demonstrated,^{8,9} which correspond to packing densities in the range of $\sim 10^9$ to $\sim 10^{11}$ cm⁻². In our study, nanopore array patterns are transferred to GaAs (001) substrates by RIE using BCl₃ through a mask of an anodized aluminum oxide membrane consisting of a self-organized nanopore array. The BCl₃ gas flow rate is 20 sccm. The pressure and power used for RIE are 15 mTorr and 100 W, respectively. Figure 1(c) presents a SEM top view image of a typical self-organized nanopore array in an AAO membrane with periodicity of 110 nm and diameter of 55 nm. This AAO membrane was used as the RIE mask to obtain a nanopore array in a GaAs substrate. Our previous studies confirm that the periodicity and the diameter of the etched nanopore arrays in GaAs are determined by the original nanopore arrays in the AAO membrane.^{10,11} The depth of the nanopores in the GaAs is controlled by controlling the RIE duration. Following the RIE step, the AAO membrane is removed chemically.

The growth of InAs QDs on the patterned GaAs substrate is conducted by solid-source MBE using As₄ and elemental group III sources. Immediately prior to being loaded into the MBE system, the nanopatterned GaAs substrates are treated by ultrasonic cleaning in deionized water. A standard thermal cleaning step is performed at 600 °C with an As beam equivalent pressure of about 1.5×10^{-5} Torr in order to desorb the surface oxide. An As-stable 2×4 reconstructed

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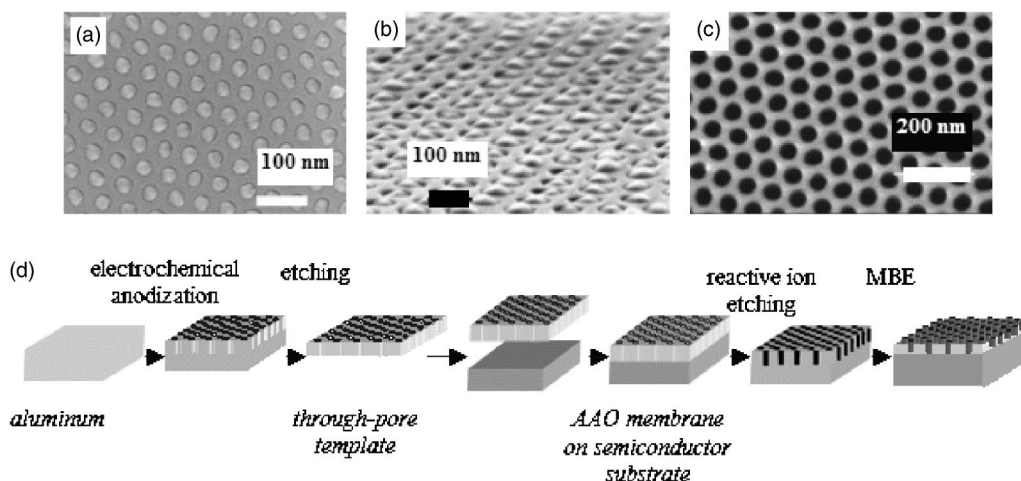


FIG. 1. Fabrication process details: (a) Scanning electron microscope (SEM) top view image of hexagonally ordered InAs quantum dot (QD) array; (b) SEM oblique view image of hexagonally ordered InAs QD array; (c) nanopore array in anodized aluminum oxide (AAO) membrane is used as the stencil for patterning; (d) schematic of fabrication process.

surface is observed by reflection high-energy electron diffraction (RHEED) to confirm the thermal cleaning effectiveness. All samples are grown under As-rich conditions. Ten monolayers (MLs) of GaAs are first deposited at 580 °C at a growth rate of 1 ML/s. It is well known in GaAs MBE that growth under these conditions will establish or reestablish a smooth surface following oxide desorption.¹² The idea of growing a thin layer of GaAs is to supply a buffer layer that partially fills in the etched topography, in order to avoid growth of the InAs directly on an ion-bombarded surface. Control of the thermal cleaning and buffer layer processes is required to prevent the complete obliteration of the etched nanopore topography, yet provide a high-quality starting surface for the QD growth. Before lowering the substrate temperature to 490 °C and starting the InAs growth, the samples are kept at 580 °C for 10 min under As overpressure. After the InAs growth, the samples are annealed for another 10 min in the MBE chamber at the growth temperature.

In order to achieve the optimal result of confining one and only one InAs QD inside each and every nanopore in the GaAs substrate, the total amount of InAs and the growth rate should be varied according to the variation of etched depth, diameter, and periodicity of the nanopores on GaAs. As a general rule, we seek an InAs growth process that would produce dots of similar density and size in conventional self-assembled SK growth. However, since not all combinations of dot size and periodicity are accessible in conventional self-assembling growth, this rule of thumb could only provide a starting point. For the sample discussed here in the XRD and SEM measurements, an amount of InAs equivalent to 35 MLs of planar growth was deposited at a rate of 0.05 ML/s on a nanopore array with periodicity of 110 nm, diameter of 55 nm, and RIE etching time of 15 min. In a second also successful sample used for TEM measurements, a similar amount of InAs was deposited at a rate of 0.2 ML/s on a similar GaAs nanopatterned substrate. The formation of QDs with relative insensitivity to different MBE growth rates implies that the nanopattern imposes an important influence on the growth kinetics and offers an advantage of easily controlling the QD size, shape, position, and density by controlling the nanopattern properties. The detailed understanding of the process window for directed-growth of ordered arrays is a subject for future study.

Figures 1(a) and 1(b) display SEM top view and oblique view images of an InAs QD array grown by this technique. It is clear that each nanopore in the substrate defines an individual InAs dot. The size distribution of the InAs QDs as measured by the standard deviation of the diameter is 9% of the mean diameter, which is 55 nm. The size and shape uniformity and long-range order of the QD array can be assessed by a 2D fast Fourier transform (FFT) of the SEM top view image as shown in Fig. 2(a) and its inset. The transform clearly demonstrates the hexagonal reciprocal lattice; the small size and high intensity of the diffraction spots are measures of the size uniformity and the spatial ordering of the InAs nanodots. For comparison, the FFT and real space images of a typical self-assembled InAs QD sample on a planar substrate grown under similar conditions are given in Fig. 2(b) and its inset. The transform in this case shows only a tendency towards a preferred size, as indicated by a fairly broad annular band, and little discernible long-range order. These results stand in marked contrast to the lattice-like image of the ordered-array sample. Images of several recently published self-assembled QD samples have been analyzed in this fashion and the results are similar to those shown, with

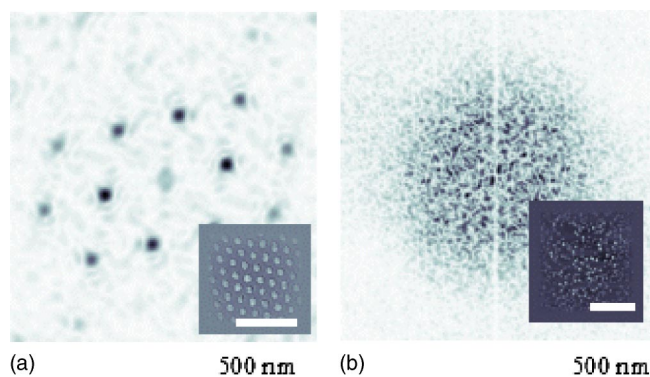


FIG. 2. Fast Fourier transform (FFT) images comparing quantum dots (QDs) fabricated by different methods. For clarity of detail in presentation, negative images are used (the highest intensities in these images are the darkest regions). The ordered InAs QD array (a) clearly exhibits a hexagonal diffraction pattern, in contrast to a typical self-assembled InAs QD array (b), with only a diffuse band of intensity and no discernible periodicities. In order to eliminate edge effects the real-space images (insets) are multiplied by a raised cosine window. Scale bars in both insets are 500 nm.

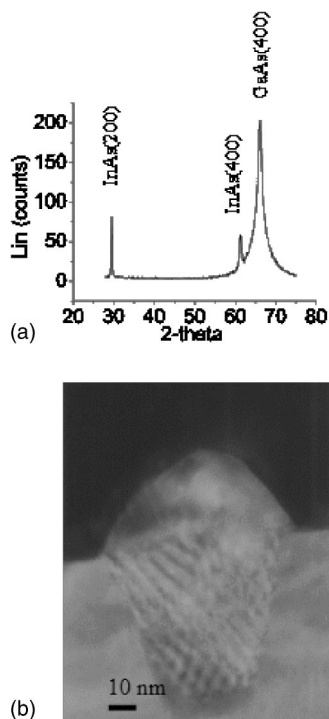


FIG. 3. Dot nanostructural details: (a) Powder x-ray diffraction pattern of the InAs quantum dots (QDs) on GaAs. The inset shows the scanning electron microscope oblique view image of the sample; scale bar is 100 nm. (b) Cross-sectional transmission electron microscope image of a single InAs QD grown inside a predefined nanopore in GaAs; scale bar shows 10 nm.

little long-range order and a relatively broad size distribution.

The as-grown highly-ordered InAs QDs are crystalline, as indicated in the powder XRD pattern [Fig. 3(a)], matching the bulk InAs peaks for InAs (002) and (004), and in the cross-sectional TEM image of an individual dot [Fig. 3(c)]. The Moiré fringes clearly seen in the TEM image suggest that the in-plane lattice parameter of the InAs QD has relaxed from the fully strained condition and thus interferes with diffraction from the GaAs substrate. The exact composition profile of the InAs QDs is not yet quantified. However, experience with self-assembled QDs suggests that interdiffu-

sion of Ga and In is to be expected, at least in the near-interfacial region.

The superior spatial ordering of directed-growth InAs QDs is attractive for development of improved devices based on QDs. There are several other evident advantages of the technology described here that combines the self-organization process in the anodization of aluminum and the enhanced self-assembly during MBE growth—easy control of QD size, spacing, density, height, and shape by controlling the properties of the AAO membranes and parameters of the RIE process; the ability to retain the long-range hexagonal ordering of the QDs; the applicability to different material systems; and the scalability of the process to the largest wafers available. When we combine those advantages with the capability of adjusting the material content in each QD by varying the MBE growth conditions, we gain a pathway for growing highly uniform and ordered QDs that is broadly enabling and applicable, as well as a dimension of freedom in the design and implementation of devices with new functionalities based on QDs.

The authors are pleased to acknowledge the ONR support for our exploration of template-assisted nanoepitaxial growth from which this work extended, and they are thankful to their Electron Microscopy Facility Manager, Anthony McCormick for his timely help in the TEM analysis.

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