Self-assembly on (111)-oriented III-V surfaces

Paul J. Simmonds and Minjoo Larry Lee

Department of Electrical Engineering, Yale University, New Haven, Connecticut 06520-8284, USA

(Received 9 July 2011; accepted 29 August 2011; published online 21 September 2011)

We demonstrate the self-assembly of tensile strained GaP into three-dimensional dots on GaAs(111)A. Size and areal density of the dislocation-free GaP dots are readily tunable with both substrate temperature and deposition thickness. GaP dot growth obeys island scaling theory, allowing us to predict dot size distributions a priori. © 2011 American Institute of Physics. [doi:10.1063/1.3640501]

The self-assembly of compressively strained nanostructures on (001) surfaces is now a well-established and fruitful research area.1–3 However, an analogous process for creating nanostructures on (111)-oriented III-V substrates is at present unavailable. Growth techniques used for traditional (001)-based self-assembly do not translate to the (111) surface; deposition of compressively strained III-V materials on (111) typically results only in the formation of flat, defective layers.2 In the absence of a reliable self-assembly technique, alternative approaches to creating (111)-oriented nanostructures have been attempted, such as substrate pre-patterning and droplet epitaxy.4,5 These however lack the simplicity and control of (001)-based self-assembly.1 Achieving dislocation-free self-assembly on (111) surfaces is of fundamental interest, but the creation of self-assembled quantum dots (SAQDs) with this orientation could also have implications for quantum optics. The piezoelectric field symmetry associated with (111)-oriented SAQDs means that fine structure splitting during biexciton recombination is expected to vanish, resulting in robust photon entanglement.4,5 Due to the respective bandgaps of the materials used in this study (at 300 K GaP = 2.26 eV and GaAs = 1.42 eV), quantum confinement of charge carriers is not expected within the self-assembled dots described here. Nevertheless, we anticipate the band offsets in other tensile strained material systems6,7 to offer quantum confinement, with the consequence that (111)-oriented SAQDs could be developed in the future using the tensile strained approach we introduce here.

Building on our earlier work regarding the spontaneous formation of three-dimensional (3D) GaP nanostructures on GaAs(110) substrates,8 in this letter, we report that self-assembly of dislocation-free dots on GaAs(111)A can be consistently achieved using tensile strain. Furthermore, we show that the Volmer-Weber (VW) growth of 3D GaP/GaAs(111)A dots obeys island scaling theory.9

During growth, biaxial strain in epitaxial materials is relaxed via two competing mechanisms.10 The first is elastic deformation, a reversible process where atoms in the film rearrange into dislocation-free 3D features for which the overall strain energy is lower than that of a flat surface. The second mechanism is plastic deformation where strain is relaxed by dislocation nucleation and glide. To obtain functional quantum dots, dislocation formation must be avoided during self-assembly. There are two predominant dislocation types that relieve strain within III-V semiconductors: 90° partial dislocations and 60° total dislocations (30° partial dislocations play a relatively minor role due to their low resolved shear and are not considered here). The behavior of these dislocations in a growing film depends strongly on the combination of sign of strain and substrate orientation.11 In particular, Kvam and Hull11 showed that the combination of tensile strain with a (111) surface prohibits the glide of 90° partial dislocations. Their model instead predicts that plastic deformation in tensile strained material on (111) must occur via the nucleation and glide of 60° total dislocations. However, both experiment and theory indicate that nucleation of these allowed 60° dislocations is kinetically limited.12–14 The existence of high-energy barriers to 60° dislocation nucleation in systems under both compressive and tensile strain is confirmed qualitatively by the routine growth of dislocation-free dots on (001) and (110) surfaces.1,8 For the purposes of this work, we inferred that by analogy, nucleation of 60° dislocations in tensile strained III-V material on a (111) surface would be similarly sluggish. If this were the case and atom mobility were sufficiently high, we predicted the existence of a window wherein elastic deformation would be the preceding strain relief mechanism, allowing dislocation-free self-assembly to occur on (111) substrates.

To test our hypothesis, we deposited tensile strained GaP onto GaAs (111)A surfaces. We chose GaP/GaAs(111)A as a test system since only the group V element differs between the deposited film and underlying surface. Furthermore, the magnitude of the lattice mismatch between GaP and GaAs is 3.7%, which is large enough to drive self-assembly in compressively strained systems.1 Samples were grown in a VEECO Modular GEN II solid-source molecular beam epitaxy system on nominally on-axis (±0.5°) GaAs(111)A (i.e., Ga-face) substrates. As4 and P2 were used as the Group V species for GaAs and GaP growth, respectively. We determined beam equivalent pressures (BEPs) for each species with a beam flux monitor, while substrate temperature (T sub) was measured with an optical pyrometer. Growth rates in monolayers (MLs) per second on GaAs(111) were calculated from reflection high-energy electron diffraction intensity oscillations on GaAs(001) substrates. We grew 60 nm homoepitaxial GaAs/GaAs(111)A buffers at 600°C with an As4/Ga BEP ratio of ~70, before annealing under As4 at 640°C for 15 min to promote surface smoothing. We then cooled the GaAs(111)A buffers to 460 °C sub ≤ 580°C, at which point the As source valve was closed for 20 s to reduce intermixing of Group V species during subsequent P-based growth. Finally, we deposited 0.0–4.3 ML GaP onto the...
GaAs(111)A buffers, under a P$_2$/Ga BEP ratio of ~12, before immediately cooling under P$_2$. We used a Veeco atomic force microscope (AFM) in tapping-mode to study surface morphologies and to compile statistics of dot size and areal density on each sample. For island scaling analysis, we surveyed a total of 500-1500 individual GaP dots from several locations on each sample. We performed plan-view and cross sectional transmission electron microscopy (PVTEM, XTEM) in a Tecnai F20 operated at 200 kV. To observe strain-contrast on the surfaces of our samples, we used PVTEM with a g = (220) two-beam diffraction condition, while to investigate internal structure, we used on-pole, high resolution XTEM along (110).

3D dots form spontaneously during the growth of GaP on GaAs(111)A surfaces. GaAs(111)A surfaces exposed to P$_2$ but not Ga (i.e., 0.0 ML GaP/GaAs(111)A) were extremely smooth [Figure 1(a)]. Although some anion exchange at the GaAs surface is likely during P$_2$ exposure, the degree of P-substitution was insufficient to affect surface morphology. In contrast, the simultaneous deposition of P$_2$ and Ga onto GaAs(111)A resulted in the formation of 3D dots via the VW growth mode [Figure 1(b)]. The GaP dots were approximately triangular, likely due to the underlying threefold symmetry of the GaAs(111)A surface. By way of comparison, we found that under identical growth conditions, deposition of GaP on GaAs(001) yielded extremely flat films with a root mean square roughness of ~0.5 nm over a 225 $\mu$m$^2$ area, and no evidence of 3D self-assembly. Given the similarities in their relative surface energies, the disparate behavior exhibited by GaP/GaAs(001) and GaP/GaAs(111)A confirms that the coupled effect of sign of strain and surface orientation plays an important role in dictating growth mode.

Of the 20–30 self-assembled GaP/GaAs(111)A dots surveyed by TEM, all were found to be free from dislocations and stacking-faults. In PVTEM, strain contrast in the GaP dots appeared as “half-moon” dark and light lobes, which is typical for coherently strained dots [Figure 1(c)]. Furthermore, we found no misfit dislocations or Moiré fringes, implying elastic deformation without the creation of dislocations. High-resolution XTEM shows atomic rows extending continuously from the GaAs substrate into the GaP dots, as emphasized by the yellow line in Figure 1(d). The absence of dislocations and other defects demonstrates that the GaP dots are coherently strained with the underlying GaAs(111)A. Our experimental observation of the dislocation-free self-assembly of GaP on both GaAs(111)A and GaAs(110) confirms Kwan and Hull’s prediction of identical dislocation behavior for tensile strained material on (111) and (110) substrates.

Having demonstrated the feasibility of dislocation-free self-assembly on (111) surfaces, we go on to show that dot size and areal density are readily controllable. We deposited 1.7 ML GaP onto a series of GaAs(111)A surfaces at 460 $\leq$ T$_{sub}$ $\leq$ 580 °C. For the growth conditions described previously, we observed 3D self-assembly only when T$_{sub}$ $\geq$ 520 °C. By raising T$_{sub}$ from 520 °C to 580 °C, we could increase both average dot height (from 3-7 nm) and average dot diameter (from 40-83 nm) [Figure 2(a)], while at the same time reducing the areal dot density (from $2 \times 10^9 \sim 7 \times 10^8$ cm$^{-2}$) [Figure 2(b)]. Raising T$_{sub}$ increases the adatom diffusion length, encouraging the formation of larger dots that minimize strain energy more efficiently than numerous small dots.

We could also manipulate dot size by changing the GaP deposition thickness at fixed values of T$_{sub}$ between 520 °C and 580 °C. Average height and diameter of the 3D dots increased in a predictable way as we raised the GaP coverage from 0.2-4.3 ML. For example, at 580 °C, we could tune average dot height from 2-7 nm and diameter from 40-140 nm [Figure 2(c)], 3D self-assembly occurred regardless of the GaP thickness used, even when we deposited only a small fraction of a monolayer. This is consistent with VW growth since a continuous two-dimensional (2D) wetting-layer cannot be present beneath the dots. As dots begin to nucleate, areal density initially increases rapidly. Again taking the series of GaP/GaAs(111)A samples grown at 580 °C as an example.
island scaling theory. We grew two series of samples at 520 °C and 580 °C. Solid lines are analytic expressions for critical cluster sizes, \( i = 1 \) and 3 in (a) and (b), respectively (Ref. 17). Insets show the unscaled distributions of dot size for the two sample sets (solid lines are guides to the eye).

[Figure 2(d)], areal density rises to a maximum of \( \sim 9 \times 10^8 \) cm\(^{-2} \) after approximately 0.4 ML GaP has been grown. The areal density then saturates and falls slightly due to dot coalescence, as seen in VW Si dots on Ge(111). 16

Scaling theory can be used to predict island size distributions \textit{a priori} and provides insight into the kinetic processes underlying dot growth. 9 Scaling theory states that \( N_s \), the distribution of dots of size \( s \), will be of the form 17

\[
N_s = \frac{\theta}{\langle s \rangle} f_s(s/\langle s \rangle),
\]

where \( \langle s \rangle \) is the mean dot size, \( \theta \) is the GaP coverage, and \( f_s(s/\langle s \rangle) \) is the scaling function, which depends only on \( s/\langle s \rangle \). The exact form of \( f_s(s/\langle s \rangle) \) depends on the critical cluster size \( i \), where \( i \) is defined as being one less than the number of atoms required to form a stable dot. In systems exhibiting island scaling, dot size distributions can be described with a single scaling function, irrespective of the deposition thickness.

The self-assembly of 3D GaP/GaAs(111)A dots obeys island scaling theory. We grew two series of samples at 520 °C and 580 °C, with GaP deposition thicknesses 0.2-4.3 ML. The insets to Figures 3(a) and 3(b) show the measured dot size distributions for each sample. After scaling using Eq. (1), the size distributions of the samples grown at both 520 °C [Figure 3(a)] and 580 °C [Figure 3(b)] collapsed onto single curves. That the two sets of scaled distributions can each be described by a single function \( f_s(s/\langle s \rangle) \), demonstrates that scaling is obeyed during 3D GaP/GaAs(111)A growth. The data scatter in Figures 3(a) and 3(b) is likely due to the limitations of AFM in measuring dot size. 18 Equation (1) applies to the GaP/GaAs(111)A system for GaP thicknesses both below and above 1 ML. We hence make the more general point that, in confirmation of earlier studies, 18,19 scaling theory can be used to describe the formation of both 2D and 3D islands.

To estimate values for the critical cluster size, we compared our scaled experimental dot distributions with theoretically derived expressions for the scaling function. 17 From the agreement between \( f_s(s/\langle s \rangle) \) (solid curve in Figure 3(a)) and our data, we infer that self-assembled GaP/GaAs(111)A dots grown at 520 °C have a critical cluster size of \( i = 1 \). Corresponding analysis reveals that \( i = 3 \) for GaP/GaAs(111)A grown at 580 °C (solid curve in Figure 3(b)). Increased critical cluster size with \( T_{\text{sub}} \) has been observed previously in other materials, 17,18 suggesting that despite the unexplored nature of 3D GaP/GaAs(111)A self-assembly, the established kinetics underpinning traditional island growth still applies.

This work represents a proof-of-concept in which we demonstrate that by harnessing tensile strain, dislocation-free self-assembly is feasible on (111) surfaces. Dot growth is readily controllable and predictable. In addition, the fact that self-assembly obeys island scaling theory provides insight into dot nucleation and growth processes. The possibility now exists that this method could be used to grow (111)-oriented SAQDs, allowing access to previously unexplored band offsets and optoelectronic properties.

We thank J. Simon and T. Krzyzewski for many useful discussions.

---