Self-assembled quantum dot transformations via anion exchange

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We report the effect of dissimilar anion anneals on the properties of layered quantum dot structures exhibiting vertical self-organization. Such anneals may provide an additional means of controlling dot properties, such as composition, size, and position. In addition, the modification of surface strain is critical to the subsequent nucleation of dots after the initial seed layer. Anion exchange may modify the strain at the semiconductor surface. We find that the effects of P_2 and As_4 anneals on InAs quantum dot size distributions are different. P_2 anneals at relatively high temperatures (350 °C) can cause the loss of the three-dimensional morphology due to surface exchange. P_2 anneals at lower temperatures (300 °C) appear to improve the uniformity of the dot size distribution. This behavior is not observed for anneals under As_4. The dot size uniformity decreases by annealing dots under As_4 at 300 °C. © *2001 American Vacuum Society*. [DOI: 10.1116/1.1385916]

I. INTRODUCTION

Self-assembled quantum dots are important for both optoelectronic and emerging electronic device applications. Control of the dot size, uniformity, and composition is critical to the effective use of quantum dots in distributed device active layers and for quantum dot-based discrete devices. We are investigating the modification of these properties via changes in growth conditions and the use of dissimilar anion (phosphorus, for example) anneals to drive surface-mediated structural changes. We have previously shown that anneals of InAs quantum dots using a phosphorus flux change the quantum dot size distribution and the composition as observed by atomic force microscopy (AFM) and x-ray photoelectron spectroscopy.[1] During anneals with dissimilar anions, surface exchange occurs and can modify the composition, and therefore strain, of the wetting layer and dots. The strain changes can, in turn, modify material reactions, as well as electronic properties of the dots. The extremes of the modifications vary from reversible three-dimensional (3D) to two-dimensional (2D) transitions (loss of dot morphology) to changes in dot shape, size, and uniformity.

II. EXPERIMENTS AND RESULTS

Our previous research focused on single-layer quantum dot structures and the dissimilar anion annealing effects on the surface morphology of quantum dots.[1] The results show that the 3D morphology changes are strongly substrate temperature dependent due to surface exchange. The morphology changes indicate that an intermixed compound with lower strain drives a transition back to 2D morphology, and an intermixed compound with higher strain enhances quantum dot formation.

In this article, our experiments focus on multilayer quantum dot structures. Our control sample consists of five layers of two or three monolayers (MLs) of InAs grown by molecular beam epitaxy. The layers are separated by 10 nm GaAs spacers. All the control samples were grown at 450 °C. Additional structures were grown with a 3 min anneal under P_2 flux or As_4 flux after each InAs deposition step. The growth temperature of the InAs and GaAs layers was 450 °C. Annealing temperatures of 300 and 350 °C were investigated. A V/III (As_4/In) flux ratio of 18 was used to grow the quantum dots. The growth rate of the InAs quantum dots was 0.67 Å/s. The As_4 beam equivalent pressures (BEP) during InAs growth and anneal were kept the same at 2.7×10^{-6} T. The BEP of the P_2 flux during anneal was 2.7×10^{-6} T. Reflection high-energy electron diffraction was used to observe the transition from a streaky pattern to a spotty pattern indicating the formation of InAs quantum dots.

AFM was used to observe the surface morphology. Table I shows the dot properties of the samples. Figure 1(a) shows the surface morphology of the control sample with 3 ML InAs. The average dot size (742 nm^2), diameter (31 nm), and density (4.99×10^{10} dots/cm^2) are similar to those of a single layer structure (average dot size = 748 nm^2, diameter = 31 nm, and density = 4.2×10^{10} dots/cm^2), but the dot size uniformity is improved significantly. A standard deviation of 664 nm^2 is observed for a single-layer structure and 303 nm^2 for a multilayer structure. This improvement is due to the vertical self-organization.[2] When the 3 ML dot layers are annealed with P_2 after the deposition of each layer, a different morphology is observed and depends significantly on substrate temperature. AFM showed a loss of 3D morphology when the dots were annealed at 350 °C. This morphology change was due to surface exchange and subsequent InAsP formation that drives the transition back to a 2D morphology. Cross-sectional transmission electron microscopy (TEM) also showed a relaxed structure (Fig. 2). When these

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TABLE I. Summary of dot distribution properties of all samples.

Sample	InAs deposition (ML)	Anion for anneal	Average size (nm^2)	Diameter (nm)	Density (10^{10} dots/cm^2)	Standard deviation of dot size (nm^2)
1	2	None	437	24	4.27	172
2	2	As_4	1036	36	2.46	195
3	2	P_2	808	32	2.62	157
4	3	None	742	31	4.99	303
5	3	As_4	1243	40	2.75	395
6	3	P_2	664	29	4.27	189

dots layers were annealed with P_2 at 300 °C, the 3D morphology was preserved [Fig. 1(b)]. Compared to the control sample with 3 ML InAs, this P_2 anneal did not significantly modify the size and density of dots, although it did improve the uniformity of the dot size from a standard deviation of 303 nm^2 for the control sample to 189 nm^2 for the annealed sample.

For the 3 ML multilayer structures, the only significant change after P_2 anneal is the uniformity of the dot sizes. The results are different for the 2 ML multilayer structures. Figure 3 shows the morphology of the 2 ML multilayer structures with and without P_2 anneal. The average dot size was increased from 437 nm^2 (diameter = 24 nm) to 808 nm^2 (diameter = 32 nm) after P_2 anneal, while the dot density was decreased from 4.27×10^{10} dots/cm^2 to 2.62×10^{10} dots/cm^2. The size and density changes can be attributed to Ostwald ripening.[3,4] Similar to the 3 ML multilayer experiments, the uniformity of the dot sizes was increased from a standard deviation of 172 to 157 nm^2 after the P_2 anneal. When comparing the 2 and 3 ML control samples, a better dot size uniformity was found for the 2 ML multilayer structure (standard deviation = 172 nm^2) in comparison to the 3 ML multilayer structure (standard deviation = 303 nm^2).

In order to determine the origin of the P_2 anneal effects on the quantum dot size distribution, more experiments were performed. In these experiments, the only difference from the P_2 anneal experiments was to use As_4 instead of P_2 while annealing the quantum dots layers at 300 °C. Compared to the control samples with no anneal, similar trends for quantum dots distribution were observed for the 2 and 3 ML multilayer structures. For the 2 ML multilayer structures, the dots size was increased from 437 nm^2 (diameter = 24 nm) to 1036 nm^2 (diameter = 36 nm), the density was decreased from 4.27×10^{10} dots/cm^2 to 2.46×10^{10} dots/cm^2, while the standard deviation of the dots size distribution was increased from 172 to 195 nm^2 after As_4 anneal. For the 3 ML multilayer structures, the dots size was increased from 742 nm^2 (diameter = 31 nm) to 1243 nm^2 (diameter = 40 nm),

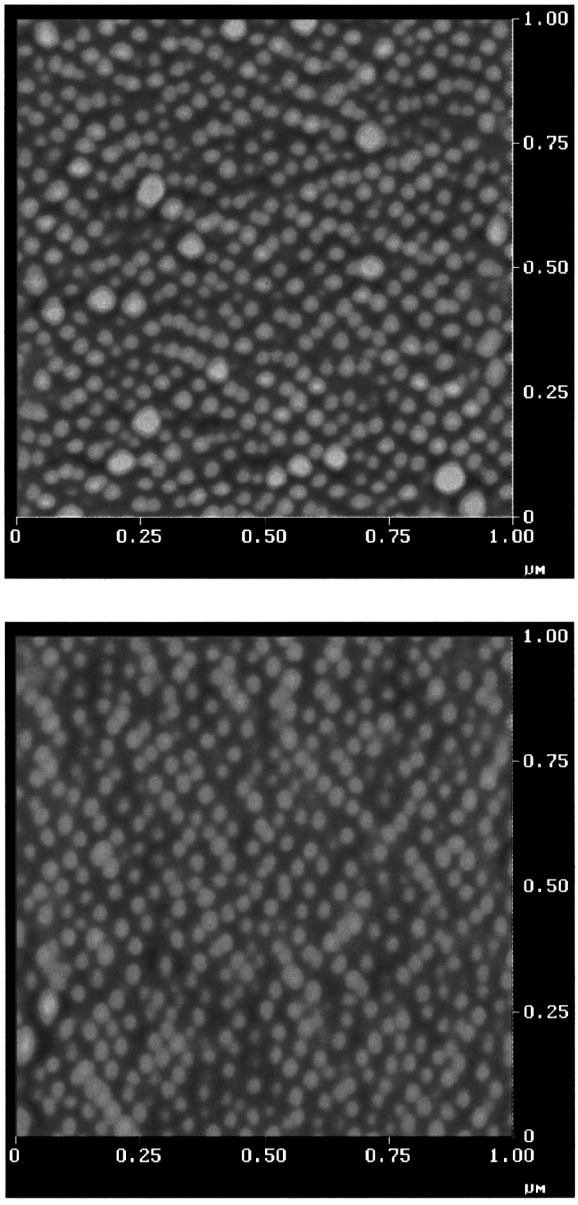

FIG. 1. (a) 3 ML multilayer structure with no anneal. (b) 3 ML multilayer structure with P_2 anneal at 300 °C.

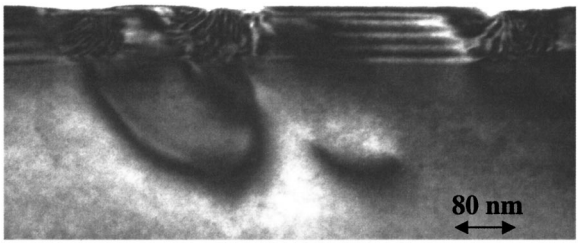

FIG. 2. 3 ML multilayer structure with P_2 anneal at 350 °C.

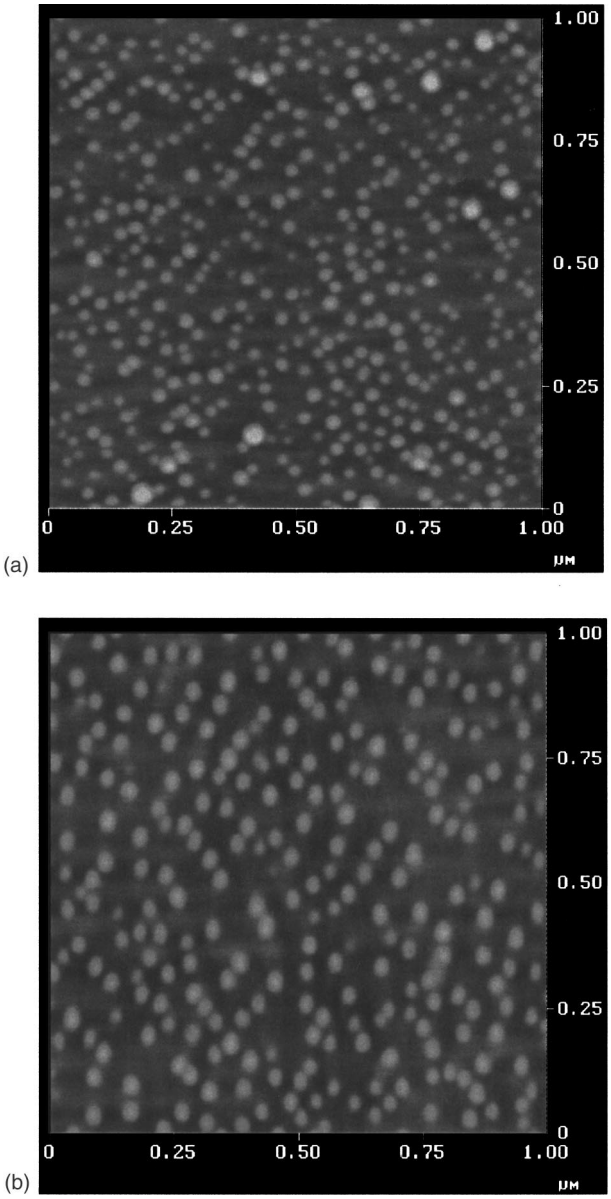

FIG. 3. (a) 2 ML multilayer structure with no anneal. (b) 2 ML multilayer structure with P_2 anneal at 300 °C.

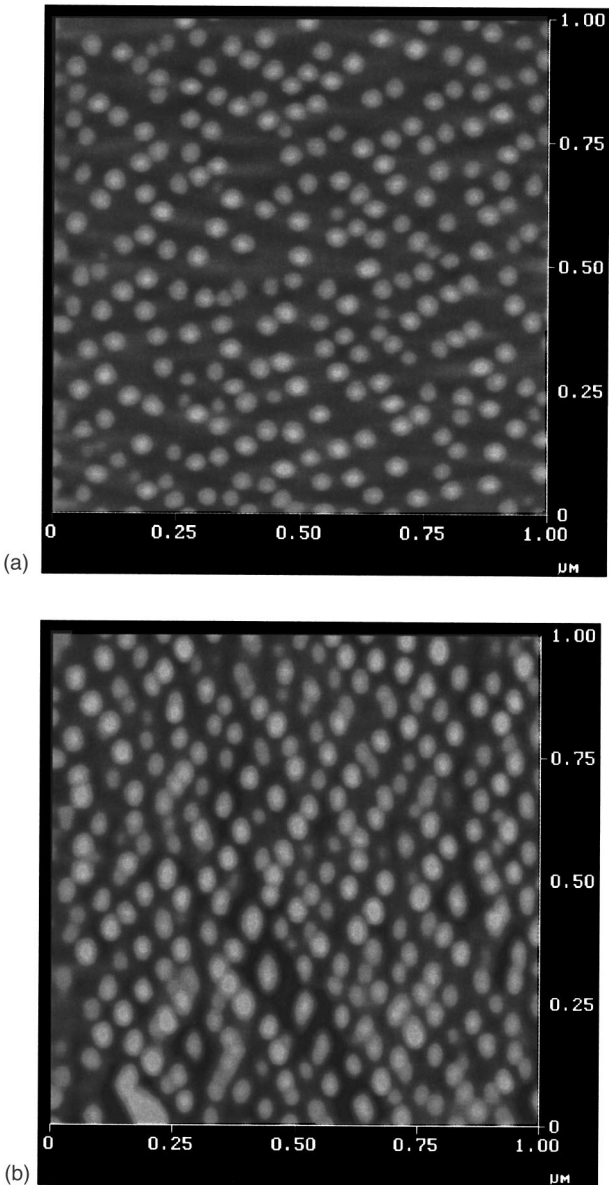

FIG. 4. (a) 2 ML multilayer structure with As_4 anneal at 300 °C. (b) 3 ML multilayer structure with As_4 anneal at 300 °C.

the density was decreased from 4.99×10^{10} dots/cm^2 to 2.75×10^{10} dots/cm^2, while the standard deviation of dots size distribution was increased from 303 to 395 nm^2 after the As_4 anneal. These changes in the average dot size and density are attributed to Ostwald ripening. Contrary to the effects of P_2 anneal on the uniformity, the As_4 anneals decrease the uniformity (Fig. 4).

From Figs. 5(a), 5(b), and 5(c), improved dot alignment appears to occur for the two annealed multilayer structures [Figs. 5(b) and 5(c)], compared to the nonannealed multilayer structures [Fig. 5(a)]. During our anneal steps, a ripening process proceeds. The larger quantum dots keep growing at the expense of the surrounding wetting layer and the smaller quantum dots. Therefore, the average dot size increases and a stronger strain field occurs. For the As_4 anneal, the large increase in dot size with each anneal step is

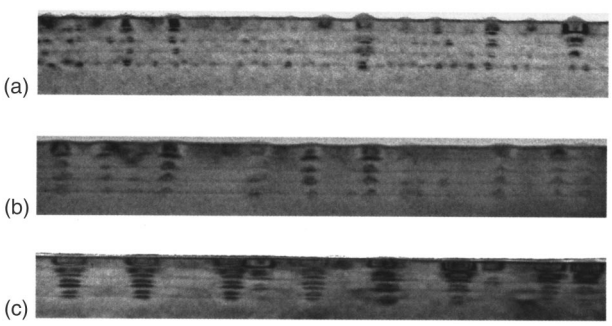

FIG. 5. (a) 2 ML multilayer structure with no anneal at 300 °C. (b) 2 ML multilayer structure with P_2 anneal at 300 °C. (c) 2 ML multilayer structure with As_4 anneal at 300 °C.

apparent. This is not desirable and may create relaxed dots. For the P_2, the change is dot size is less dramatic.

III. SUMMARY

Anion anneals have different effects on the quantum dot size distributions and vertical self-assembly. Phosphorus anneal at 300 °C can enhance the uniformity of the dot size distribution for both 2 and 3 ML multilayer structures. TEM shows vertically aligned dots structure after annealing at 300 °C and a relaxed structure after annealing at 350 °C. Arsenic anneal increases the dots size, decreases the dots density, and decreases the uniformity of quantum dots distribution. More experiments will be performed by high resolution TEM to understand the compositional change for phosphorus anneal.

ACKNOWLEDGMENTS

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