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Published in: Applied Physics Letters

DOI: 10.1063/1.4796036

Published: 01/01/2013

Citation for published version (APA):
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Citation: Appl. Phys. Lett. 102, 113103 (2013); doi: 10.1063/1.4796036
View online: http://dx.doi.org/10.1063/1.4796036
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i11
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The disintegration of GaSb/GaAs nanostructures upon capping

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(Received 26 October 2012; accepted 6 March 2013; published online 19 March 2013)

Atom probe tomography and cross-sectional scanning tunneling microscopy show that GaSb/GaAs quantum dots disintegrate into ring-like clusters of islands upon capping. Band transition energies calculated using an 8-band $k\cdot p$ model of the capped dots with the observed dimensions are consistent with emission energies observed in photoluminescence data. These results emphasize the need for full three-dimensional characterization to develop an accurate understanding of the structure, and thus the optical properties, of buried quantum dots. © 2013 American Institute of Physics.

http://dx.doi.org/10.1063/1.4796036

Semiconductor quantum dots (QDs) are of particular interest for electronic applications such as photovoltaics,1–4 lasers,5,6 and charge storage devices.7 Specifically, GaSb/GaAs QDs are of interest because of their type-II band alignment, which is believed to increase charge separation and reduce radiative recombination, making them a primary candidate for intermediate band solar cells.3 For device applications, QDs are capped following their formation. The specific materials used for the dot and capping layer8 as well as the particular capping conditions (e.g., temperature, growth rate)9,10 can affect the size, shape, and composition of buried QDs. For example, dissociation and a change in QD shape for GaSb/GaAs QDs has been observed due to intermixing between the capping material and the QD.11–18 This redistribution of the QD material upon capping affects the optical properties of the QDs by creating large variations in the size and composition of the capped QDs, leading to an undesirable increased photoluminescence (PL) linewidth.13,16,19–21

Understanding the three-dimensional structure of buried QDs and the subsequent effects on their optoelectronic properties is fundamental to determining ways to either exploit or eliminate changes in shape and/or composition that occur to GaSb/GaAs QDs during capping. Several studies have investigated capped QD composition and morphology by using two-dimensional analytical techniques such as transmission electron microscopy (TEM)14,16,17 and cross-sectional scanning tunneling microscopy (XSTM).11–16 To date, capped GaSb/GaAs nanostructures have been hypothesized to evolve into rings.11–17 XSTM, which images a single $x$-$z$ plane of the nanostructure, shows that many, though not all, of the QDs change into pairs of small islands separated by 5 to 10 nm of pure GaAs. The pairs of small islands have been interpreted as the body of the ring with a GaAs-filled center between them.11–15 There are also some reports of this ring structure in TEM studies,14,16,17 but because TEM relies on projections through the thickness of the nanostructures, it is difficult to distinguish the pairs of islands as seen in XSTM. More recently, XSTM has shown that small clusters of GaSb may form upon capping.15 Given this ambiguity, the range of structures observed in capped GaSb still needs to be further understood.

These nanostructures can be studied using atom probe tomography (APT), which provides three-dimensional information about their shape and composition. Combining XSTM and APT provides a clearer understanding of the structure of the buried QDs and offers further explanation for the optical properties observed for these nanostructures. In this study, we present analysis of buried GaSb/GaAs QDs via XSTM and APT and discuss the effects of compositional and morphological changes incurred during capping on the optoelectronic properties of the nanostructures as seen in the QD PL and band transition energy calculations.

A multilayer GaSb/GaAs sample with eleven QD layers was grown by molecular beam epitaxy on a GaAs(100) substrate for PL and atomic force microscopy (AFM) analysis. A 500 nm thick undoped GaAs buffer layer was grown at $T = 590$°C at a rate of 1.0 monolayer (ML) s$^{-1}$. The sample was then cooled to $T = 460$°C for deposition of 2.3 ML of GaSb at a rate of 0.3 ML s$^{-1}$ and a V/III ratio of 2, immediately followed by a 20 nm GaAs spacer layer grown at the same rate. QDs were formed via the Stranski-Krastanov growth mode whereby a thin, uniform GaSb layer called the wetting layer (WL) is initially formed and QDs nucleate to decrease the overall strain once a critical thickness of GaSb is deposited. All temperatures were measured using an optical pyrometer. The topmost (eleventh) layer remained uncapped for analysis by AFM for comparison to the capped nanostructures. PL measurements were taken at $T = 10$ K in a helium flow cryostat at 424.5 μW using a HeNe laser operating at 633 nm. The PL spectrum was collected using a 0.75 m spectrometer with a 150 G/mm reflection grating and a single channel InGaAs detector.
A second sample was grown for XSTM and APT under the same conditions as the first (i.e., same growth rates, temperatures, and amount of GaSb deposited for the QDs). However, the number of GaSb/GaAs QD layers was reduced to five and the spacer thickness increased to 50 nm to reduce strain build up in order to get a smoother cleaved surface for XSTM. Additionally, the buffer and topmost GaAs layer were p-doped to a concentration of $3 \times 10^{17} \text{cm}^{-3}$. XSTM measurements were performed at $T = 77 \text{K}$ under ultra-high vacuum conditions ($p \leq 3 \times 10^{-11} \text{mbar}$). Electrochemically etched tungsten tips were operated at constant current mode in the STM. The samples were cleaved in-situ to scan over atomically flat and clean (110) surfaces. The APT volumes were prepared using a standard focused ion beam lift-out technique and annularly milled to a tip diameter of approximately 100 nm at the apex. Analysis was done in a Cameca LEAP 4000 operated between 20 and 33 K in voltage pulsing mode with a pulse fraction of 15%. Six APT volumes, each consisting of one or two QD layers, were obtained. Reconstruction parameters (i.e., image compression factor and the value of the evaporation field) were selected to yield flat GaSb layers and to match the layer spacing of 50 nm. Volumes where only a single GaSb layer was imaged were reconstructed using the same evaporation field, and only minor changes were made to the image compression factor to ensure a flat GaSb layer.

Uncapped surface QDs were imaged by AFM to compare the size and areal density of the buried dots to their uncapped precursors. Figure 1 shows an AFM image of the uncapped QDs and histograms of the dot diameter and height size distributions. The number of bins for the histograms was determined based on the square root of the total number of data points. The average diameter and height of the uncapped QDs are 42 ± 5 nm and 3.6 ± 0.9 nm, respectively, and the areal density of QDs is $3.5 \times 10^{10} \text{cm}^{-2}$. Figure 2 shows the PL spectrum from the eleven-layer QD sample. The GaAs substrate peak is at 1.49 eV, the WL peak is at 1.36 eV, and the QD peak is centered at approximately 1.13 eV. The QD peak appears to have a shoulder at approximately 1.18 eV, and it has two lower energy peaks at 0.98 and 1.07 eV, all of which are unexpected because the size distribution of the uncapped QDs as measured by AFM appears to follow a normal distribution (Figures 1(b) and 1(c)). Instead, it is likely that the inhomogeneity in the PL results from changes in the QD shape and size upon capping.

The buried QDs were analyzed by XSTM in order to gain information about their size, shape, and composition after capping. XSTM images of the various types of nanostructures observed are shown in Figure 3. Three primary structures can be identified via XSTM: compact QDs, pairs of small islands, and clusters of islands, in agreement with other reports. The formation of island pairs and clusters was attributed to the relaxation of strain caused by the lattice mismatch of the GaSb and GaAs, and the clusters were assumed to be an intermediate structure. Assuming that the island pairs and clusters form from dissociation of compact QDs and are, therefore, counted as single nanostructures, the areal density of nanostructures as measured by XSTM is approximately $2 \times 10^{10} \text{cm}^{-2}$, which is in good agreement with the density of the uncapped QDs as measured by AFM. Figure 3(a) shows an XSTM image of a compact QD with a truncated pyramidal shape. Figures 3(b) and 3(c) show island pairs with spacing between islands of approximately 2 and 15 nm, respectively. In addition to compact dots and rings, clusters similar to those reported by Smakman et al. are also observed. Figures 3(d) and 3(e) show examples of clusters, which we define as groups of small islands that appear to arise due to the dissolution of QDs upon capping. These clusters differ from the island pairs in their number of segments and/or the spacing between segments, which may be as small as a few atoms.

APT analysis of the nanostructures in three-dimensions is used in conjunction with the XSTM data to gain further understanding of the morphology of the buried QDs. The nanostructures observed by APT are consistent with those observed in the XSTM images. Figure 4 shows a three-dimensional plot of one of the APT volumes showing two GaSb nanostructures. Figure 4 also shows several contour plots of Sb concentration for some of the capped GaSb nanostructures analyzed by APT. The three-dimensional plot in Figure 4(a) shows only Sb atoms. An iso-concentration...
surface of approximately 9% Sb is highlighted. The contour plots in Figures 4(b)–4(e) are created by slicing through the center of the nanostructures. The concentration scale is the same for each contour plot and is based on three-dimensional iso-concentration surfaces. A voxel size of 0.5 × 0.5 × 0.5 nm³ and a delocalization distance of 3 nm are used. The choice of these parameters only affects the smoothness of the profiles and not the local concentrations that each region represents. The images in Figure 4 are intended to be qualitative. Lower Sb concentrations in Figure 4 are displayed in color from darker (lower %Sb) to lighter (higher %Sb). Higher Sb concentrations in the compact QD in Figure 4(c) are simply shown in white with black contour lines. One-dimensional profiles are obtained along cylinders of 1.5 nm diameter with a bin width of 1.5 nm and shown in Figure 5 to provide quantitative values of Sb concentration. The locations of the line profile through the nanostructures are indicated by (1), (2), and (3) in Figure 4. In contrast to what is suggested by the XSTM images, all examined APT volumes show that there are only two major types of buried nanostructures: compact QDs and ring-like clusters of small islands. Compact QDs account for approximately one third of the nanostructures observed while clusters of small islands account for the rest. Each cluster is comprised of two to four islands, which vary in size and shape. The concentration of Sb between the islands of each cluster also varies. For example, there is more Sb present between the islands in the cluster in Figure 4(b) than there is between those shown in Figures 4(c) and 4(d) (note that Figure 4(d) shows two side-by-side clusters of small islands). Nonetheless, for all clusters of small islands, the concentration of Sb is consistently lowest at their center, providing a “ring-like” shape. From the line profiles in Figure 5, we see that the concentration of the compact QDs reaches approximately 50% Sb at the center and decreases outward due to intermixing during capping. However, the small islands within the clusters are much more dissociated, and the Sb concentration at the center in (3) is on the order of that of the WL.

Cross-sectional contour plots of Sb concentration shown in Figures 4(f) and 4(g) are taken from slices along different x-z planes through the same ring-like cluster of small islands (Figure 4(e)). These cross-sectional contours provide a view of the sample analogous to what is imaged using XSTM. By comparing Figures 4(f) and 4(g), it becomes obvious that the position of the cross-section within the cluster of small islands greatly affects the interpretation of the image when viewed solely along a specific x-z plane. For example, Figure 4(f) shows a cluster very similar to the XSTM image in Figure 3(e), while Figure 4(g) shows a pair of small islands very similar to the XSTM image in Figure 3(c) even though these two cross sections taken from Figure 4(e) are only a handful of atomic spacings apart. It is clear, therefore, that GaSb QDs do not simply form rings upon capping as previously hypothesized. Rather, the QDs disintegrate into smaller islands. This fact can only be determined without ambiguity using a three-dimensional characterization technique such as APT. One drawback of this method, however, is the small number of nanostructures that can be analyzed at one time. Therefore, other nano-scale techniques like XSTM and TEM are necessary in order to analyze a larger number of small islands.
nanostructures. This provides improved statistics on the size and type of nanostructures present. For instance, in this work, each APT sample contained two to four complete nanostructures (i.e., nanostructures completely encompassed within the APT volume as opposed to partially imaged nanostructures at the edge of the volume), while TEM and XSTM can provide an order of magnitude more structures per image. Combining these techniques provides a clearer interpretation of the three-dimensional morphology of the capped nanostructures than any one technique alone.

The evolution of the QDs during capping significantly affects the optical properties of the buried nanostructures as evidenced by the PL (Figure 2). We propose that the broadening of the QD PL peak results from a distribution of compact QDs and clusters of small islands formed during capping. We estimate the effect of the compact QDs and clusters of smaller islands by comparing their transition energies, calculated using an 8-band \( k\cdot p \) model.\(^2\) In the calculation, the shape of the compact QD and the smaller islands within the clusters are defined as spherical caps. The diameter and height of the compact QDs, estimated based on the APT data, are 21 nm and 3.6 nm, respectively. The diameter and height of the small islands are 13 nm and 2.3 nm, respectively. The strain distribution in GaSb/GaAs nanostructures was calculated using the valence force field model of Martin.\(^2\) With the atomic displacement of minimal total energy condition, the deformation potential of the structure was calculated\(^2\) to construct the strain Hamiltonian. In this step, the conduction band, heavy-hole, light-hole, and spin-orbit bands of GaSb are shifted down to 530 meV to obtain consistency with the experimental value of the transition energy within the QDs\(^2\) and the conduction band offset of the QDs.\(^2\) The total 8-band \( k\cdot p \) Hamiltonian\(^2\) was numerically solved by the finite difference method to obtain the hole states in the valence band. The transition energies calculated were 0.365 and 0.300 eV for the compact QDs and smaller islands, respectively, resulting in PL peaks at 1.155 and 1.220 eV, as indicated by the solid and dashed lines in Figure 2. These energies are in reasonable agreement with the broadening of the PL peak and support the hypothesis that QD disintegration upon capping leads to a broadening, and in this case, a bimodal distribution of QD sizes due to the presence of compact QDs and small islands. The origin of the two lowest energy peaks remains uncertain. Based on these calculations, it is unlikely that the two lowest energy peaks also result from inhomogeneity in QD size because the dot dimensions required for emission at such low energies are larger than that of their uncapped precursors, let alone accounting for any size reduction resulting from intermixing during capping. We observe that these two peaks have a narrow line width and are approximately equidistant from the two peaks between 1.1 and 1.2 eV, suggesting that they may arise due to impurity states within the QDs, although their origin is yet unknown.

In conclusion, we have demonstrated by three-dimensional analysis via APT that GaSb/GaAs QDs disintegrate into ring-like clusters of small islands upon GaAs capping with approximately two to four islands per cluster. These ring-like clusters appear as closely spaced island pairs or clusters when imaged by XSTM, demonstrating the need for multiple corroborative techniques in order to fully understand the structure of buried QDs. The presence of clusters and compact dots results in a broad size distribution of nanostructures and in this particular case, a bimodal size distribution. This is evident in the split QD PL peak and corroborated by the calculated transition energies for the compact QDs and small islands within the clusters using an 8-band \( k\cdot p \) model.

This material is based upon work supported as part of the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0000957.


