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Height stabilization of GaSb/GaAs quantum dots by Al-rich capping

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GaSb quantum dots (QDs) in a GaAs matrix are investigated with cross-sectional scanning tunneling microscopy (X-STM) and photoluminescence (PL). We observe that Al-rich capping materials prevent destabilization of the nanostructures during the capping stage of the molecular beam epitaxy (MBE) growth process and thus preserves the QD height. However, the strain induced by the absence of destabilization causes many structural defects to appear around the preserved QDs. These defects originate from misfit dislocations near the GaSb/GaAs interface and extend into the capping layer as stacking faults. The lack of a red shift in the QD PL suggests that the preserved dots do not contribute to the emission spectra. We suggest that a better control over the emission wavelength and an increase of the PL intensity is attainable by growing smaller QDs with an Al-rich overgrowth.

It was demonstrated recently that a significant number of GaSb nanostructures grown on GaAs disintegrate under the influence of high local strain fields and Sb segregation in the growth direction during capping with GaAs.1–5 That is, the strain induced by capping causes lateral out-diffusion of Sb from the quantum dot (QD) core.6 A strategy to prevent disintegration would be to curtail Sb out-diffusion. Al-containing compounds in general have higher bond strengths, and thus lower surface diffusion rates than those containing Ga, while maintaining nominally the same lattice parameter. Therefore, QD height retention should improve with the addition of Al to the capping layer. This material system could be interesting for intermediate band solar cells7–9 and flash-memory applications.10, 11 In the latter case, the QDs are coupled to a two-dimensional hole gas to obtain very fast read and write times.12, 13 A large hole localization energy is then crucial for a long storage time. Recently it was shown that the hole localization energy for GaSb/GaAs QDs is increased when Al-rich capping material is used compared to pure GaAs.14 In this work, we present a cross-sectional scanning tunneling microscopy (X-STM) and photoluminescence (PL) study on GaSb QDs in a GaAs matrix grown by molecular beam epitaxy (MBE), overgrown with Al-containing III-V capping materials.

All of the QD samples were grown in Stranski-Krastanov mode using MBE on GaAs (100) substrates. Each sample had an undoped 500 nm GaAs buffer layer, grown at a rate of 1.0 monolayer (ML)/s. Before QD formation, samples were cooled to \( T = 460 \) °C, as measured by an optical pyrometer, to deposit 2.3 ML of GaSb at a rate of 0.3 ML/s with a V/III ratio of 2. The resulting QD concentration was approximately \( 5 \times 10^{10} \) cm\(^{-2}\). The original uncapped dot height as measured by atomic force microscopy (AFM) was \( 4 \pm 1 \) nm. Immediately afterward, the capping layer was

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FIG. 1. STM images taken at $V = -4.00$ V and $I = 250$ pA. Typical examples of GaSb nanostructures grown on GaAs, capped with (a) 50 nm GaAs, (b) 1 ML of AlAs followed by 50 nm GaAs, (c) 3 ML of AlAs followed by 50 nm GaAs, and (d) 20 nm of Al$_{0.50}$Ga$_{0.50}$As followed by 30 nm of GaAs. (b) and (c) represent intact QDs, and (a) and (d) are disintegrated nanostructures. (e) Topography and (f) current images of a QD capped with 1 ML AlAs, with a structural defect emanating from the nanostructure.

grown, and four different capping layer compositions were used: 50 nm of GaAs, 1 ML of AlAs with 50 nm of GaAs, 3 ML of AlAs with 50 nm GaAs, and 20 nm Al$_{0.50}$Ga$_{0.50}$As with 30 nm of GaAs. The capping layers were grown at 0.3 ML/s as well, with the exception of the AlGaAs layer which was grown at 0.6 ML/s. All of the material was annealed for 10 min at the growth temperature and quenched.

The samples for X-STM contain seven QD layers: one layer with GaAs capping as a reference and two layers of each other capping material. They were cleaved revealing $\{110\}$ surfaces under ultra-high vacuum (UHV) conditions in an Omicron LT-STM, operated at a pressure of $p \leq 4 \times 10^{-11}$ mbar and a temperature of $T = 77$ K. Electrochemical etching was used on polycrystalline W wire to obtain atomically sharp tips. These tips were subsequently annealed and sputtered with Ar under UHV conditions. The samples for PL each contained ten layers of QDs of a single capping composition. Cooled to $T = 10$ K, they were measured using a Coherent Mira Ti:Sapphire tunable laser at $\lambda = 845$ nm with a spot size of $5 \mu$m. An 850 nm filter was placed in the collection path and emission was collected using an InGaAs detector. The samples were excited below the bandgap energy of GaAs to prevent saturation of the wetting layer by the bandgap emission peak.

Examples of topography images of the GaSb nanostructures are shown in Fig. 1. At the chosen tunneling conditions, the STM technique primarily images the filled states of the group V elements. The contrast is thus mainly determined by the local dangling bonds of the chemically different As and Sb atoms, which appear darker and brighter, respectively. The influence of group III atoms on this contrast is weak due to the fact that they are nearest neighbors to the group V atoms. Furthermore, for surface group V elements only a fraction of the three nearest neighbor Ga atoms are replaced by...
Al atoms, further reducing the contrast for the Al in the thin capping layer. Unfortunately the sample did not allow stable tunneling at positive bias voltages, which would allow tunneling directly in the empty dangling bonds of the group III atoms. Additionally, the effect of strain is also visible as a bright contrast in the images representing outward relaxation around the QDs. The size and purity of the QD leads to a high build-up of local strain, which is partially relaxed outwards from the surface when the sample is cleaved. Because of the high local strain around the QDs, some of the images contain cleaving artifacts, i.e., material that is ripped out or left behind when the sample is cleaved.

For this work we analyzed 389 QDs recorded by X-STM and determined their morphology and size. A substantial part of the imaged nanostructures is very pure and the original uncapped QD height is retained, see, for example, Figs. 1(b) and 1(c). However, quite frequently the QDs are disintegrated and appear as segmented structures, visible in Fig. 1(a), or ring-shaped objects, visible in Fig. 1(d). There is almost no intermixing visible in the GaSb/GaAs QDs, which is clear from the absence of any alloy fluctuations and the pure Sb content visible in our X-STM images. This is different from InAs/GaAs QDs, where intermixing plays a more important role in ameliorating any high local strain that could potentially destabilize the nanostructures. We also observed the appearance of structural defects around the larger, intact QDs, such as those visible in Figs. 1(e) and 1(f).

The QD height distributions for the various capping materials are presented in Fig. 2. We categorize a nanostructure as disintegrated when at least 10% of the intact dot shape is affected. We estimate a 10% error in the statistical analysis, mainly due to the fact we are using a 2D imaging technique to classify 3D nanostructures. Clearly, the Al-rich capping materials have a large effect on the growth, because the average dot height shifts from around 3.1 nm for GaAs capping to around 4.5 nm for the other three Al-rich capping materials, which matches with the original uncapped QD height. Disintegrated QDs are on average much lower, because the GaSb migrates from the top of the nanostructures during growth, leaving behind only a part of the original shape. The height distributions thus reveal that the use of Al-rich capping materials leads to the better preservation of the original dot height after capping. The percentage of retained structures increases from 52% in the case of GaAs capping to 70% by capping with 1 ML AlAs. With 3 ML AlAs and AlGaAs capping, the height retention is increased to 79% and 83%, respectively.

The data show that including Al in the capping layer does in fact result in higher, less eroded QDs, likely due to the reduction of lateral Sb diffusion during overgrowth. But removing QD height reduction as a mechanism to reduce the strain around the capped nanostructures results in the appearance of another strain relieving mechanism. A side-effect of the dot preservation is that structural defects appear around some of the QDs, primarily around the taller, intact QDs. A structural defect that appears close to a QD is shown in Figs. 3(a) and 3(b). Mismatch between atomic rows is visible along two ⟨111⟩ directions that start around the QD and end in a single point in the cross-sectional plane. The area on top of the QD is relaxed inward with respect to the surrounding surface, suggesting tensile strain in that region. Inspection of Fig. 2 reveals that the defects are present in 9% of the structures for 1 ML AlAs, 17% for 3 ML AlAs and up to 22% for AlGaAs capping, compared to 11% for GaAs capping. The data show that they occur especially near the QDs that retain their full height, which means that the Al-rich capping layers contain the most defects.

The structural defects occur because of the large lattice mismatch between the almost pure GaSb QD and the GaAs substrate. We suggest a structural atomic model for this type of defect, which is displayed in Fig. 3(c). This ball and stick model represents the ⟨110⟩ plane imaged by X-STM. The bigger dots are the atoms in the surface layer accessible to the STM. 1 ML below there is another layer of atoms indicated by the smaller dots. In this model, we propose that there are several dislocations present at the interface between the GaAs and the GaSb QD. This assumption is consistent with published reports that show that these interfacial misfit dislocations can occur during growth of GaSb QD nanostructures. Due to the misfit dislocations and the high amount of strain, the surrounding GaAs or AlGaAs does not grow in perfect registry with the capping layer directly on top of and in the immediate vicinity of the QD. Thus, the GaAs lattice grown on top of the QD is displaced 1 ML in the [001] direction with respect to the surrounding GaAs matrix, effectively
forming a stacking fault.\textsuperscript{19} In 3D, the stacking fault forms a displaced \{111\} plane, which terminates in a defect or when it meets another stacking fault. The latter is the situation displayed in the model and in the observed X-STM images where two stacking faults meet and annihilate.

The change in QD height, as well as the presence of stacking faults, is expected to alter the optical properties of these films. The PL measurements depicted in Fig. 4 are consistent with the structural trends observed in the X-STM results. Similar to other GaSb/GaAs QD research, the wetting layer is strong relative to the QD peak.\textsuperscript{20–22} The energy positions of the wetting layer peak for the Al-containing capping are blue-shifted to between 1.35 and 1.36 eV, with respect to the GaAs capped sample that emits at 1.32 eV. Since the Al capped layers retained the QD height

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FIG. 2. Height distributions of the QD nanostructures for the various capping materials. The histograms bin size is chosen to be one lattice constant of GaSb, equal to 0.61 nm.
FIG. 3. STM images taken at $V = -4.00$ V and $I = 250$ pA. Example of a defect near a QD capped with AlGaAs, visible in (a) a topographic and (b) a current image. (c) Structural model showing the (110) plane of the material, similar to the X-STM images. Around the QD, several misfit dislocations are visible that result in two stacking faults on top, extending into two different ⟨111⟩ directions.
FIG. 4. PL measurements of ten layers of QDs capped with GaAs, 1 ML of AlAs, 3 ML of AlAs, and AlGaAs. The samples were excited below the GaAs bandgap to isolate wetting layer and QD emission. Laser power density was approximately $2.6 \times 10^3 \text{ Wcm}^{-2}$. The spectra are normalized to the wetting layer peak.

better than the GaAs capped layer, it is expected that less Sb out-diffused from the nanostructures in these samples. This means that the Al-rich overgrowth would result in a thinner wetting layer, which emits at higher energies. The uncertainty in our X-STM analysis of the wetting layer profiles does not exclude the shift in PL. Recent atom probe tomography (APT) measurements were able to accurately determine concentration profiles in GaSb/GaAs wetting layers of various heights and the corresponding PL indeed revealed a blue-shift for thinner wetting layers.\(^{22}\) Additionally, the Al-rich capping material creates a larger energy barrier for the wetting layer with respect to the GaAs overgrowth. The resulting stronger hole confinement also contributes to a blue-shift in the wetting layer PL. Despite the observed increase in QD size with Al capping, there is no significant change in QD peak position compared to the GaAs reference sample. This is surprising because larger QDs should emit at lower energies. We suggest that only smaller QDs, those with the same average height as in the GaAs capped sample, are contributing to the optical emission. To test this, Nemo3D’s Quantum Dot Lab tool was used to simulate the ground energy state of strained GaSb QDs at $T = 10 \text{ K.}^{23}$ Pyramidal QDs with diameters of $5 - 16 \text{ nm}$, heights of $2.4 - 6.0 \text{ nm}$, and aspect ratios of $0.2 - 0.5$ were simulated. The simulation shows that QDs that are $2.5 - 4.0 \text{ nm}$ tall can emit within the observed experimental ranges between $1.10$ and $1.25 \text{ eV}$. QDs greater than $4.5 \text{ nm}$, the average height of QDs in the Al-containing samples, are not predicted to emit at all. This result is consistent with the view that only the smaller QDs can contribute to the PL emission.

To obtain high uniformity GaSb QD layers with a good optical quality, we propose the growth of relatively small QDs capped with Al-rich material. This combines the benefit of preserving the original dot height by suppressing Sb out-diffusion while lowering the overall amount of strain, reducing the chance to inject strain relaxing structural defects that negatively affect the optical properties. Another approach would be to grow intermixed GaAsSb QDs or use an intermixed AlGaAsSb capping layer to reduce the strain and prevent stacking faults.

In summary, we show that the addition of Al into the GaAs capping layers result in higher, more intact GaSb QDs. This is due to the suppression of strain driven lateral Sb diffusion, As/Sb exchange and Sb segregation. A consequence of the QD erosion process is that misfit dislocations and stacking fault formation are enhanced during overgrowth. The optical properties of the studied nanostructures are consistent with the observed structural trends, showing lower intensity emission from the optically active smaller QDs. We suspect the growth of smaller QDs or the use of As intermixing in the nanostructures or Sb intermixing in the capping layer can create a material with a good optical quality.
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