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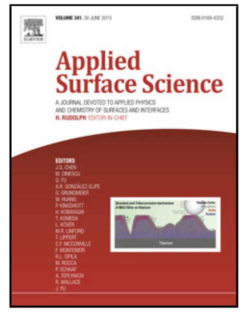

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Effect of an *in-situ* thermal annealing on the structural properties of self-assembled GaSb/GaAs quantum dots

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Abstract

In this work, the effect of the application of a thermal annealing on the structural properties of GaSb/GaAs quantum dots (QDs)[1] is analyzed by aberration corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)[2] and electron energy loss spectroscopy (EELS)[3]. Our results show that the GaSb/GaAs QDs are more elongated after the annealing, and that the interfaces are less abrupt due to the Sb diffusion. We have also found a strong reduction in the misfit dislocation density with the annealing. The analysis by EELS of a threading dislocation has shown that the dislocation core is rich in Sb. In addition, the region of the GaAs substrate delimited by the threading dislocation is shown to be Sb-rich as well. An enhanced diffusion of Sb due to a mechanism assisted by the dislocation movement is discussed.

Keywords

GaSb, quantum dot, scanning transmission electron microscopy, thermal annealing

Introduction

Nowadays, much effort is dedicated to research in the semiconductor field because of the importance of these materials in nanotechnology. The use of epitaxial nanostructures such as QDs provides additional properties like the 3D confinement, allowing the improvement of photonic[1] and electronic devices [2] as well as the development of new material designs [3, 4]. In particular, Type-II GaSb/GaAs QDs have potential applications in lasers [5], photodiodes [6] and novel memories [7], and can largely extend the spectral response beyond the visible out towards 1.4 µm providing a near optimum band gap for concentrator solar cell applications [8]. However, the growth of this material has the inconvenience of the high lattice mismatch between GaSb and GaAs, 7.8%. This frequently causes the appearance of dislocations [9], which produce a detriment in the structural quality and, consequently, in the optoelectronic properties of

[1] Quantum dots
[2] High-angle annular dark-field scanning transmission electron microscopy
[3] Electron energy loss spectroscopy

the devices. Dislocations introduce additional electronic states within the band gap, leading to nonradiative recombination phenomena. The application of a post-growth thermal annealing is a typical practice in order to improve the material quality [10]. Two types of thermal treatments are normally applied in these materials: *ex-situ* and *in situ* ones. Ex-situ thermal treatments (e.g. rapid thermal annealing) typically involves temperatures in the range of 650 to 800 °C, and can potentially affect the entire sample. Indeed, in such procedures the sample is normally covered by a GaAs substrate to avoid damaging the surface. In this paper, we analyze a sample of GaSb/GaAs QDs where the annealing method used is much more subtle: annealing is performed in-situ at just 580°C after the growth of a thin cap layer. Application of a conventional ex-situ technique to this a sample would have a very drastic and damaging effect on the quantum dots which are near the surface of our sample. The effect of these thermal annealing on the structural quality of semiconductor materials is frequently measured indirectly, through the analysis of the optoelectronic properties of the material [11-13]. Some works have been published where the effect of the application of a thermal treatment to semiconductor materials is analyzed by direct measurements in order to study the structural quality of the sample, for example, by conventional transmission electron microscopy [10, 14]. These analyses provide information on the nanometer scale. For example, the application of a thermal annealing in InAs/GaAs QDs has shown to reduce the density of threading dislocations and to have some effect on the size of the nanostructures [14]. However, only the analyses at atomic column resolution can provide a complete picture of the effect of a thermal annealing in order to obtain a better understanding of this thermal treatment. In this work, we analyze by aberration corrected HAADF-STEM and EELS the effect of an in-situ thermal annealing on the structural quality of heterostructures of GaSb/GaAs QDs.

Experimental

The samples studied consist of nanostructures of GaSb grown on a GaAs (001) substrate by molecular beam epitaxy. Initially, a GaAs buffer layer with a thickness of 250-350 nm has been grown at 580ºC at a growth rate of 1 MLs^{-1}. Then, the substrate temperature has been reduced to 490ºC for the deposition of the GaSb with a deposition rate of 0.3 MLs^{-1} during 7 s, reaching a thickness of 2.1 ML. After that, the structures have been thinly capped with ~10 nm of GaAs at 430ºC with a growth rate of 1 MLs^{-1}. Then, an *in-situ* annealing is applied to the second sample at 580ºC during 2 min under As_2 flux. A conventional method has been used to prepare the samples in cross section for the analysis by STEM. This method consists of mechanical thinning using SiC sandpaper and Ar^+ milling using a precision ion-polishing system. In order to obtain a very thin electron transparent and clean sample, the beam energy during the milling process is controlled carefully. At the beginning of the thinning process the beam energy is 3.5 kV and in the last step of the process the energy is reduced to 2 kV in order to have a smooth surface. Once the sample is electron-transparent and with the objective of eliminating organic compounds from the sample, a plasma clean is applied for 5 minutes. The sample has been studied by HAADF-STEM using a NION UltraSTEM 200 5th order probe aberration-corrected electron microscope, with a Nion cold field emission gun, working at a beam voltage of 200 kV and with sub-Ångstrom resolution at this acceleration voltage. EELS measurements have been taken in the same microscope with a GATAN Enfinium dual EELS spectrometer.

Results

Fig. 1 a shows a HAADF-STEM image of a GaSb QD in the sample where no annealing treatment has been applied. (This sample has been studied in the two perpendicular [110] directions in order to corroborate that the observed nanostructures actually have the shape of QDs). In HAADF-STEM, the intensity of the images is related to the average atomic number (Z) in the material. For this reason, Sb-rich columns present more intensity in the image (Sb has higher Z than As) and the GaSb QDs appear brighter. In order to investigate the morphology and dimensions of the nanostructures, an intensity map has been obtained from the image using the *qHAADF* method as presented by Molina *et al*. [15]. For this, the methodology explained in [15] has been followed, using as the integration area the region corresponding to a single atomic column in the image. Fig. 1 b shows a map of the ratio between the integrated intensity measured at the atomic columns divided by the average integrated intensity in the GaAs substrate taken as a reference (I.R., *intensity ratio*). As it can be noticed in this map, the QD has an elongated shape, with reduced height. The analysis of different QDs in this sample (approx. 20 QDs) has shown that the morphology and dimensions are very similar among the nanostructures. In particular, average heights of 6.7±1.3 nm and diameters of 20±3 nm have been measured. It should be mentioned that the obtained intensity maps have not been used for the quantification of the Sb in the QDs because of the 3D shape of these nanostructures. TEM images are the result of a projection of a volume of the sample in a 2D plane, and therefore the projection of the atomic columns in the area of the 3D nanostructure may contain a mixture of atoms contained in the nanostructure and others located in the capping layer. Because of this, the method described in Molina el al. cannot offer precise results for the analysis of 3D nanostructures. Fig. 1 c shows a HAADF-STEM image of a GaSb/GaAs QD in the second sample in which an *in-situ* thermal annealing has been applied. Fig. 1 d shows the corresponding intensity ratio map. As it can be observed in both figures, the morphology of the QD after the annealing is different than in those without the thermal treatment. The average height of the QDs found in this sample is 4.5±0.5 nm and the average diameter is 25±3 nm, therefore the QDs are more elongated. Also, it is worth to mention here that the Sb (responsible for the higher intensity columns) is more concentrated inside the QD in the non-annealed sample.

For the sample with annealing process, the interface GaSb-GaAs is not well defined and the distribution of the high intensity columns in Fig. 1 d indicates that some Sb diffusion has taken place in all directions (as expected), causing intermixing with the surrounding As atoms. The out-diffusion of elements from epitaxial nanostructures has been suggested to take place in semiconductor materials when an annealing process is applied. In multilayers of InAs/GaAs QDs, it has been reported that annealing at 700ºC produces a decrease of the size of the QDs likely due to the diffusion of In, increasing the number of nanostructures. For very high annealing temperatures (800ºC), most of the QDs disappear because In atoms diffuse into the wetting layer [14]. Also, studies in InGaAs/GaAs QDs have shown that annealing at 750ºC reduces the strain field in the QDs because of the reduction in their size, probably due to the diffusion of In to the wetting layer [11]. In our high-resolution analysis, we have obtained experimental evidence of Sb out-diffusion from the QDs, as shown by the intensity ratio map in Fig. 1 d.

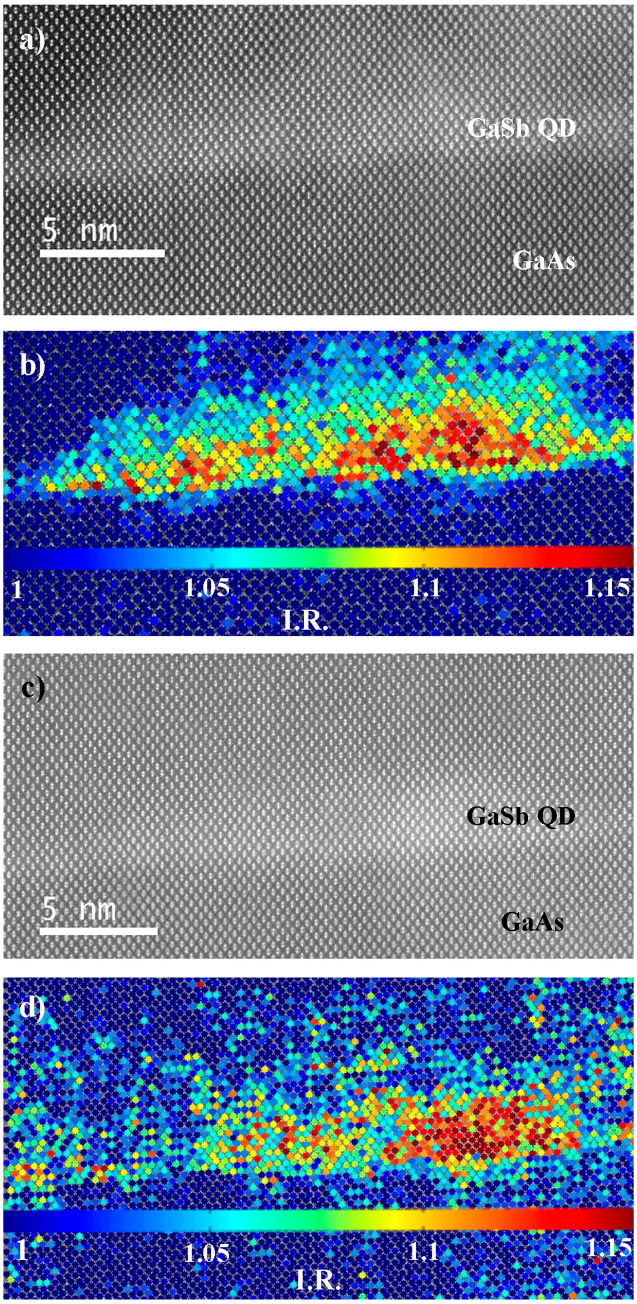

Fig. 1 HAADF-STEM images of a GaSb QD in the sample without (a) and with an *in-situ* thermal annealing (c). (b) and (d) are the integrated intensity ratio maps from the images in (a) and (c), respectively.

It should be noted that the analysis of some QDs in the sample with no thermal annealing has shown the presence of misfit dislocations. A detailed characterization of these dislocations is published elsewhere [16]. In the present work, it is found that in the sample with the heating treatment, misfit dislocations are not observed in the QDs. The analysis by TEM does not allow for a good statistical study of the structural features in a sample, given that a reduced area of the material is analyzed. Because of this, in this study we cannot conclude that misfit dislocations have completely disappeared during the thermal treatment, but our results show a clear reduction of their density after this process. This indicates a better structural quality of the sample because of the annealing. Many studies have showed that heating treatments improve the crystal quality of semiconductor heterostructures. For example, in AlGaN thin films [10] and in InAs/GaAs QDs[14], a reduction in the density of threading dislocations after the heating process has been reported.

In the sample studied in this work, although misfit dislocations have not been observed, it should be highlighted that scarce threading dislocations have been found in the structure. Fig. 2 a shows a HAADF-STEM image of the annealed sample, where the GaSb layer is marked with a white arrow. As it can be observed, a threading dislocation crossing the GaSb layer towards the substrate is found in the image, likely formed from the gliding of a pre-existing misfit dislocation during the thermal treatment. A closer look at the image shows that a brighter contrast is observed in the GaAs substrate in the region delimitated by the dislocation than in the external area. This could be attributed to a higher amount of Sb in that region due to the diffusion of this element during the thermal treatment. It should be mentioned that the dislocation also shows an intense contrast in the image. In this case, that contrast cannot be attributed to compositional changes because HAADF images are sensitive to the strain in the material [17, 18]. The highly disordered region at the core of the dislocation introduces a large strain responsible for the observed contrast. Because of this, and in order to analyze the distribution of Sb in this region, the analysis by EELS of the composition in the area around the observed dislocation has been carried out.

Fig. 2 b shows EELS spectra taken at the region corresponding to the $M_{4,5}$ edge of Sb (528 eV) from the GaAs substrate (1), from the core of the dislocation (2) and from the GaAs area delimitated by the dislocation (3), at the positions marked in Fig. 2 a). From the spectra, no Sb is detected in the GaAs substrate (position number 1 in Fig. 2 a)), as expected. However, a clear Sb signal is found in position 2, corresponding to the dislocation core, and indicating a preferential diffusion of Sb towards this defect. Our analysis do not allow the quantification of the Sb composition at the dislocation core because the signal obtained comes from the interaction of the electron beam with the dislocation core but also with the GaAs region above and below in the electron-transparent thin foil. Despite this, the increase of the Sb composition at the dislocation is clear. This finding can be explained by the strain in the heterostructure. Sb atoms have larger size than As atoms, therefore GaSb-rich zones are in compression when grown on a GaAs substrate. The core of a dislocation is a distorted region, therefore the diffusion of Sb atoms towards this area reduces the compression and thus the strain in the material..

The composition at dislocation cores is not a routine measurement due to the high spatial resolution needed to obtain this information. Only the development of aberration correctors to be used in advanced TEM techniques such as HAADF and EELS has allowed acquiring information of the composition distribution around these defects. For example, in $SrTiO_3$ direct evidence for a local coordination of edge-sharing TiO_6 octahedra at the dislocation cores has been obtained using these techniques [19]. In epitaxial $BaTiO_3$ thin films the atomic ratios of O/Ti and Ba/Ti have been found to decrease at the dislocation core [20]. In our study, the dislocation core has shown to have a different composition than the surrounding material, but also the GaAs region delimited by the dislocation line has an unexpected composition distribution. Thus, as it can be observed in Fig. 2 b, the spectra taken at point 3 in the HAADF image shows the presence of Sb, although in smaller amount than at the dislocation core.

Interestingly, our results suggest that the gliding of a dislocation is a mechanism that facilitates the diffusion of Sb atoms outside the QDs. Sb atoms may diffuse towards the dislocation core for the strain reasons explained above. The movement of the dislocation may leave behind the Sb-enriched region observed by EELS. The enhancement of the Sb diffusion produced by this mechanism assisted by the dislocation movement can be prejudicial for the optoelectronic properties of the material. In GaAs/AlGaAs QDs, the interdiffusion Al–Ga is suggested to be responsible for modifications of the photoluminescence band during a thermal annealing [21]. The diffusion of In atoms from $In_{0.5}Ga_{0.5}As$ QDs to the GaAs layer near the heterointerface during a thermal annealing has been considered as the cause for the blue-shift of the PL emission of the material [11]. Therefore, the effect of the application of a thermal annealing on the structural properties of the GaSb/GaAs QDs studied seems to be two-fold, as besides the advantages associated to the observed reduction in the misfit dislocations density, a strong Sb diffusion out of the QDs is evidenced, both locally close to the GaSb-GaAs interfaces, and in a larger scale assisted by the dislocation glide. The mechanism of Sb diffusion assisted by the dislocation movement found in this study should be considered in order to understand the effect of a thermal annealing on the optoelectronic properties of semiconductor heterostructures.

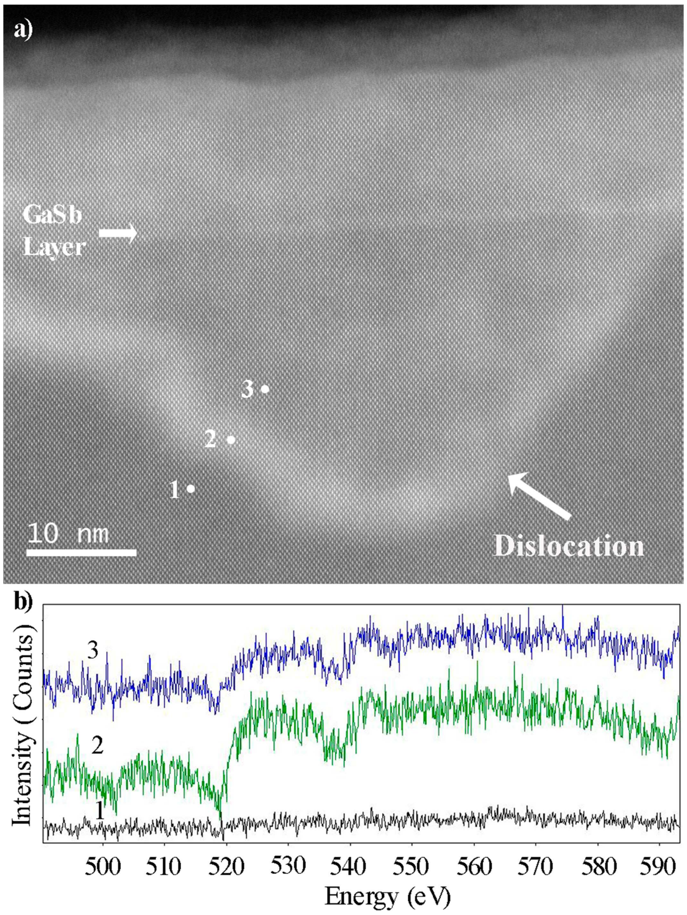

Fig. 2 a) HAADF-STEM image of a threading dislocation; b) EELS profiles from the GaAs substrate (1), from the dislocation core (2) and from the GaAs region delimited by the dislocation (3).

Conclusion

The application of an *in-situ* thermal annealing to a heterostructure of GaSb/GaAs QDs has changed the morphology of the buried nanostructures. The thermal annealing process causes a reduction of the QDs height and some intermixing at the interfaces, due to the diffusion of Sb. Even, the density of misfit dislocations has been strongly reduced, and threading dislocations have been observed. The composition at the core of a threading dislocation has been analyzed, and it has been found to be Sb-rich. Interestingly, the region of the GaAs substrate delimited by the threading dislocation has been found to be Sb-rich as well, although in a small amount in comparison to the dislocation core. Our results suggest that the diffusion of Sb is enhanced by the dislocation glide, and an Sb rich region is left behind the dislocation movement. This enhanced diffusion can deviate the optoelectronic properties of the material from the designed ones, therefore this new mechanism should be taken into account in the effect of a thermal annealing on the structural properties of the material.

Acknowledgements

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