ELSEVIER

Journal of Crystal Growth 150 (1995) 311–316

JOURNAL OF CRYSTAL GROWTH

In-situ fabrication of three-dimensionally confined GaAs and InAs volumes via growth on non-planar patterned GaAs(001) substrates

A. Konkar, K.C. Rajkumar, Q. Xie, P. Chen, A. Madhukar *, H.T. Lin, D.H. Rich

Photonic Materials and Devices Laboratory, Department of Materials Science and Engineering, University of Southern California, Los Angeles, California 90089-0241, USA

Abstract

Three-dimensionally confined GaAs/AlGaAs and InAs/GaAs structures on ⟨100⟩ oriented square mesas patterned onto GaAs(001) substrates are realized, in-situ, via size-reducing molecular beam epitaxy. Two stages of mesa top pinch-off involving ~ {103} and subsequently {101} side facets are revealed. GaAs and InAs quantum boxes with lateral linear dimensions down to 40 nm and confined by AlGaAs and GaAs, respectively, are reported. For InAs, the strain relief in mesas is found to enhance the well known ~ 2 ML thickness for three-dimensional island formation on unpatterned substrates to, remarkably, > 5 ML for mesa size ~ 75 nm. Cathodoluminescence emission from the InAs on the mesa top attests to its good optical quality.

Semiconductor nanostructures confined in three dimensions on a sub-100 nm length scale have attracted much attention these days, as they are expected to exhibit novel electrical and optical properties [1]. Growth on patterned substrates which utilizes the differences in the growth rates on different facets can be used to achieve such structures in a single growth step [2–4]. It is reported that Rajkumar and co-workers succeeded in utilizing substrate encoded size-reducing epitaxy (SESRE) [2] for the synthesis of three-dimensionally quantum confined (i.e. quantum box) structures on nonplanar patterned GaAs(111)B. The size reducing feature of this approach eliminates the need for creating mesas via patterning on the desired nanostructure size scale, making conventional lithographic patterning on micron length scales followed by wet chemical etching suitable for subsequent nanostructure fabrication via growth alone. In this paper we report two applications of SESRE in molecular beam epitaxial growth on patterned nonplanar GaAs(001) substrates for realizing *three*-dimensionally confined structures: (i) GaAs volumes confined by AlGaAs [3], and (ii) InAs volumes confined by GaAs barriers.

The basic criterion for uniform shrinkage of the mesa top during a size-reducing growth is that atoms migrate from all the sidewalls to the mesa top at equal rates giving higher growth rate on the mesa top than on the adjacent sidewalls.

* Corresponding author.

0022-0248/95/$09.50 © 1995 Elsevier Science B.V. All rights reserved
SSDI 0022-0248(94)00903-1

SESRE achieves this by encoding (patterning) the substrate so as to yield appropriate sidewalls upon growth, and maintaining growth conditions which promote adatom migration from the sidewalls to the mesa top. It has been shown [3,4] that growth on GaAs(001) square mesas with edges along ⟨100⟩ instead of ⟨110⟩ directions can satisfy this basic condition, thus allowing the realization of *three*-dimensionally confined structures on (001) substrates. In this paper we show that the mesa top experiences two stages of pinch-off related to the initial formation of {101} side facets followed by the formation of ~{103} facets. The ~{103} facets, though formed later, cause an early pinch-off and the {101} facets subsequently take over and cause a second pinch-off. In the case of the growth of the lattice mismatched (~7%) InAs on GaAs, the strain relief arising from small mesa sizes is shown, for the first time, to enhance the 2 ML InAs critical thickness for three-dimensional island formation on unpatterned substrates to > 5 ML for mesa sizes of ~75 nm.

GaAs(001) substrates were patterned along ⟨100⟩ directions using conventional photolithography and wet chemical etching. An array of 10 μm side squares was defined photolithographically followed by etching in 4:1:20::NH_4OH:H_2O_2:H_2O for about 2–4 min to give square mesas with ~3–4 μm long edges oriented along ⟨100⟩ and ~2–3 μm in depth. The growth structure for the study of the mesa size evolution consisted of a size-reducing buffer of four periods of 1500 Å GaAs/500 Å $Al_{0.3}Ga_{0.7}As$ followed by a 20 ML GaAs/40 ML $Al_{0.3}Ga_{0.7}As$ multiple quantum well. The total growth thickness was 1.5 μm. The starting mesa size varies from 3 to 4.5 μm. This mesa size variation allows us to investigate different stages of pinch-off in the same growth run since it is expected that at the same stage of deposition mesa pinch-off occurs later on mesas with larger starting lateral size. In the following we present examples of the two stages of pinch-off. Fig. 1a shows a post-growth scanning electron microscope (SEM) image of the growth

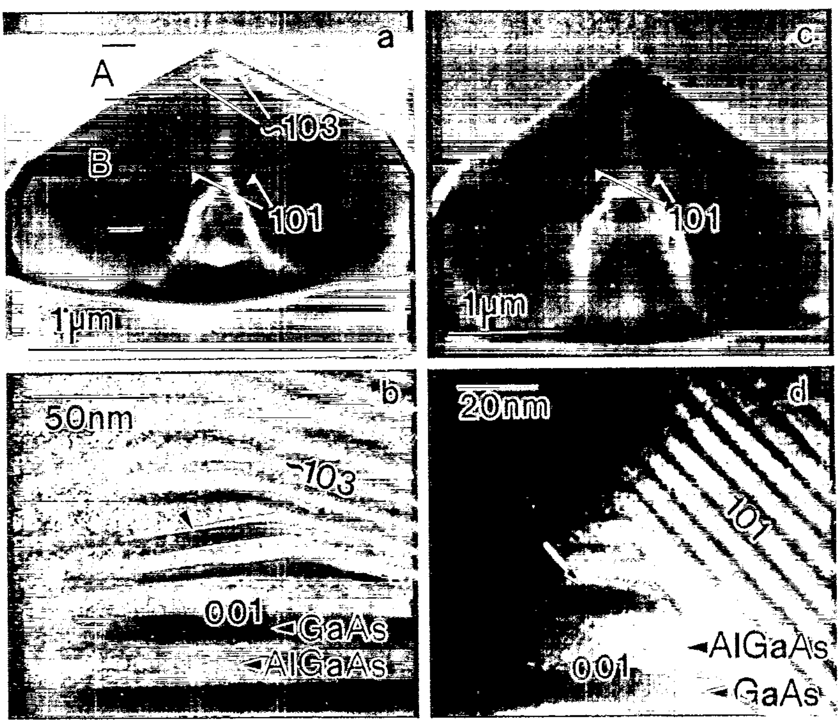

Fig. 1. Panels (a) and (b) show, respectively, SEM side view taken along [1$\bar{1}$0] with a tilt of 75° about [110] and (002) reflection, ⟨010⟩ azimuth XTEM image of a mesa pinched off by the ~{103} sidewalls. Panels (c) and (d) show the corresponding images for a mesa pinched off by {101} sidewalls.

on mesas with a starting mesa top size of 4.2 μm for which the growth is stopped at the first stage of mesa pinch-off by ~{103} sidewalls. It can be seen that in the lower part (marked B) the mesa is surrounded by {101} sidewalls while, at the top (marked A), the mesa is surrounded by ~{103} sidewalls. Fig. 1b shows a cross-sectional transmission electron microscope (XTEM) image of the mesa top. The marker layers clearly show the shrinkage of the (001) mesa top by the ~{103} facets. The two sidewalls and the (001) mesa top layers are not clearly imaged simultaneously, since the (001) and the two ~{103} planes do not belong to a single zone axis. Fig. 1c shows a post-growth SEM image of a growth on mesas with a starting size of 3 μm in which growth was allowed to proceed to the second stage of pinch-off by the {101} sidewalls. This corresponds to the second stage of the pinch-off. It can be seen that the whole mesa is now surrounded by {101} facets extending all the way to mesa pinch-off and no ~{103} facets are observed. The inner structure, as revealed by the XTEM image of the mesa top in Fig. 1d, shows that the (001) mesa top reappears after the first stage of pinch-off by ~{103} sidewalls and is now pinched by the {101} sidewalls. We note that the GaAs volumes close to pinch-off in both the stages are vertically confined by AlGaAs barriers. For the final stage this is marked by the arrow in Fig. 1d. The lateral confinement in the final stage of pinch-off due to the negligible growth on the {101} sidewalls is also clearly seen in Fig. 1d. The lateral dimensions (440 Å (bottom) and 275 Å (top)) and the height (100 Å) of the GaAs volume are in the quantum confinement regime. As for the earlier pinch-off stage, the lateral confinement is not obvious since the ~{103} sidewalls are not clearly imaged for the reason noted earlier.

The stages of sidewall evolution leading to the first stage of mesa pinch-off by ~{103} facets are illustrated in Figs. 2a–2d. Upon growth, initially {101} sidewalls form and start to shrink the (001) mesa top (Fig. 2b). As growth continues, ~{103} sidewalls get initiated near the (001) mesa top (Fig. 2c). The ~{103} sidewall edges shared with (001) mesa top form a rhombus (Fig. 2c). This might be a reflection of the equivalency of only the diagonally opposite corners of the starting mesa. With continued growth, both the {101} and the ~{103} sidewalls grow and the (001) mesa top is now reduced in size by the ~{103} sidewalls, finally leading to (001) pinch-off (Fig. 2d). The second stage of pinch-off is illustrated in Figs. 2e and 2f. After the pinch-off by ~{103}, continued growth results in shrinkage of the ~{103} sidewalls by {101} sidewalls. At a certain point the ~{103} facets start evolving into facets

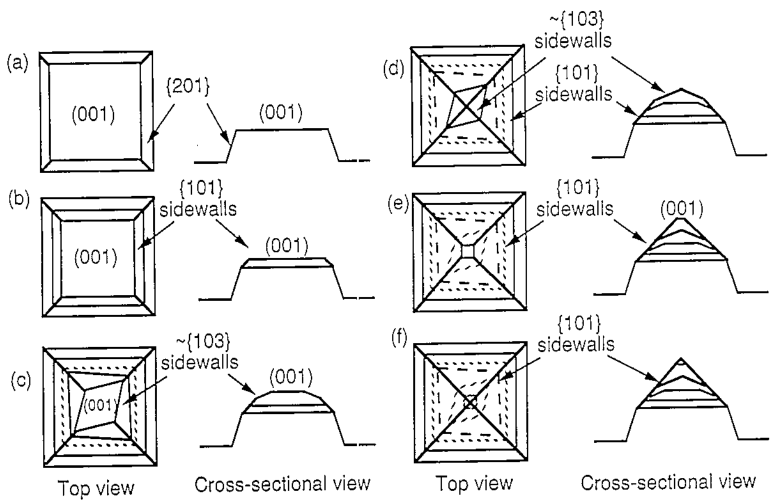

Fig. 2. Schematic diagram illustrating the evolution of the mesa top at various stages of growth. Though not shown in the schematic diagram to maintain clarity, there is some growth on the sidewalls.

closer to (001), finally creating a (001) segment between the {101} sidewalls (Fig. 2e). This (001) segment is pinched-off by {101} sidewalls with further growth (Fig. 2f).

Another point regarding pinch-off by {101} sidewalls concerns the growth rate variation with the (001) mesa top size. If the adatom migration rate from the sidewalls to the mesa top were independent of the mesa top size, then the growth rate on the mesa top will be expected to increase with decreasing mesa top size. This is observed in the early stages of growth. However, when the mesa top size is < 2000 Å, the growth rate on the mesa top begins to decrease with decreasing mesa top size. This has been previously observed close to the pinch-off stage in MBE growth on mesas on GaAs(111)B [2] and in metalorganic chemical vapor deposition (MOCVD) grown GaAs via selective epitaxy on masked GaAs(111)B substrates [5]. Such a variation of growth rate with reducing mesa top size close to the pinch-off point is related to the change in the net lateral adatom migration and possibly the changes in effective growth condition on such extremely small mesa top sizes induced by the lateral migration itself. The details of this study will be presented elsewhere. Interestingly, such a growth rate variation is helpful in reducing the size fluctuations in the confined structures arising from the variations in the starting mesa size and thus plays an important role in the success of fabricating quantum boxes via growth on nonplanar patterned substrates.

On our substrates, stripes oriented along ⟨010⟩ direction are also patterned along with the square mesas. The {103} facet formation is not observed on the striped mesas. Lopez et al. [6] have observed formation of both {103} and {101} sidewalls upon growth on such *striped* mesas, but report that the formation of the {103} facets is suppressed for either high growth temperatures or low arsenic pressures. We surmise therefore that presumably our growth conditions, found useful for quantum box creation, correspond to these of Lopez et al.'s growths for quantum wires. In our growths, the lack of {103} sidewalls on the stripes, but their presence on the square mesas, might be due to the adatoms migrating from the sidewalls to the square mesa top interfering in the regions close to the corners of the square. If so, its consequence would not be evident in the case of long striped mesas, but would be easily seen for growth on square mesas.

We next turn to the lattice mismatched system, $In_xGa_{1-x}As$ on GaAs(001), in which the lattice mismatch can be as high as 7% for $x = 1$. The

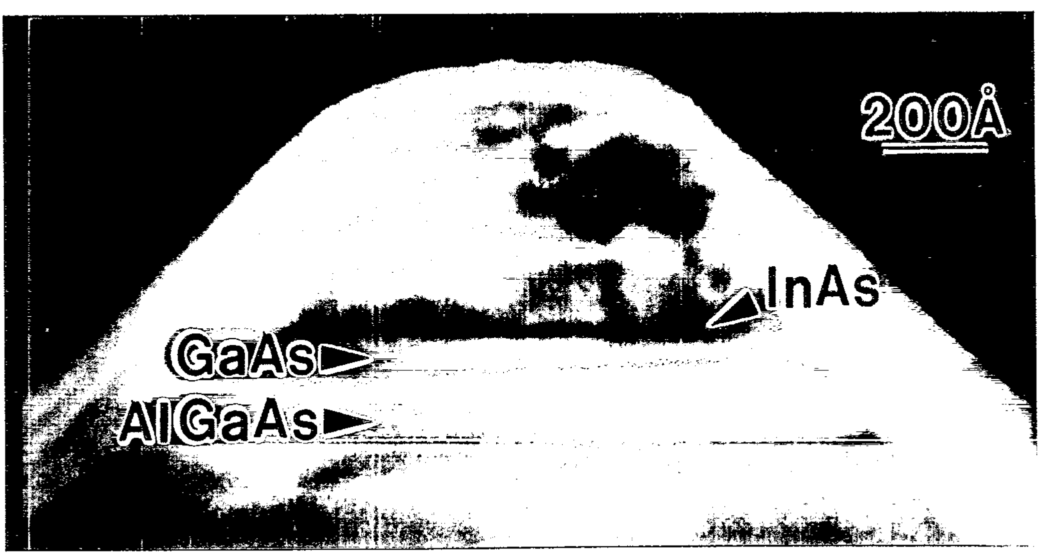

Fig. 3. (002) reflection, ⟨010⟩ azimuth TEM image of a mesa top showing InAs layer.

well-known tendency for 3D island formation at high lattice mismatch has recently attracted attention since it was shown [7] that coherent 3D islands can be realized. Such islands provide a means of quantum box fabrication on planar substrates [8,9], as demonstrated in the paper by Xie et al. [10] in these proceedings. This approach, however, presents the challenge [9] of being able to form a spatially uniform array of islands of equal size in the quantum box regime. Depositing InGaAs on an array of size-reduced mesas is expected [9] to circumvent the above problem and the use of the binary InAs avoids any ambiguities introduced due to potential alloy segregation effects if InGaAs is grown. We have thus deposited binary InAs on size-reduced GaAs(001) square mesas with edges along ⟨100⟩. Since the confinement in the final stage of pinch-off by {101} is more evident, the InAs was deposited prior to this final pinch-off stage. In this work 3.5 ML of InAs was delivered after growth of ~1 μm thick size-reducing multilayered GaAs/AlGaAs buffer on mesas with starting size of ~3.2 μm. The InAs was buried under an 80 ML thick GaAs cap containing two 10 ML thick AlGaAs marker layers. Fig. 3 shows a XTEM image of the mesa top. This TEM image has been obtained without any TEM specimen preparation and making use of the fact that a small region close to the mesa top is thin enough for electron transparency, thus allowing imaging of the layers within the pinch-off region [11]. The image shows clearly the InAs layer on a ~75 nm (001) top surrounded from all sides by GaAs barrier. The apparent InAs thickness on the mesa top is 8–9 ML, but discounting for the strain broadening of the contrast it is conservatively ≥ 5 ML. Though beyond the critical thickness (~2 ML) for 3D island formation on planar GaAs(001), remarkably there is no evidence of islanding. This increase in the critical thickness for InAs grown on such size-reduced mesa tops, demonstrated here for the first time, is consistent with strain relief provided by small mesas which has previously been shown [4,12] to be effective in significantly enhancing the critical layer thickness for misfit dislocation formation when the growth mode remains 2D (i.e. layer-by-layer).

To determine the optical activity of the InAs on the mesa top, cathodoluminescence (CL) experiments on this sample were performed. Fig. 4a shows a typical area-averaged CL spectra taken from the mesa top region. Two peaks are seen. The sharp peak at 900 nm is from an InGaAs quantum well deposited at the start of the buffer for growth rate calibration. The broad peak (FWHM ~60 meV) centered at 1120 nm is from the InAs deposited to form the quantum box near

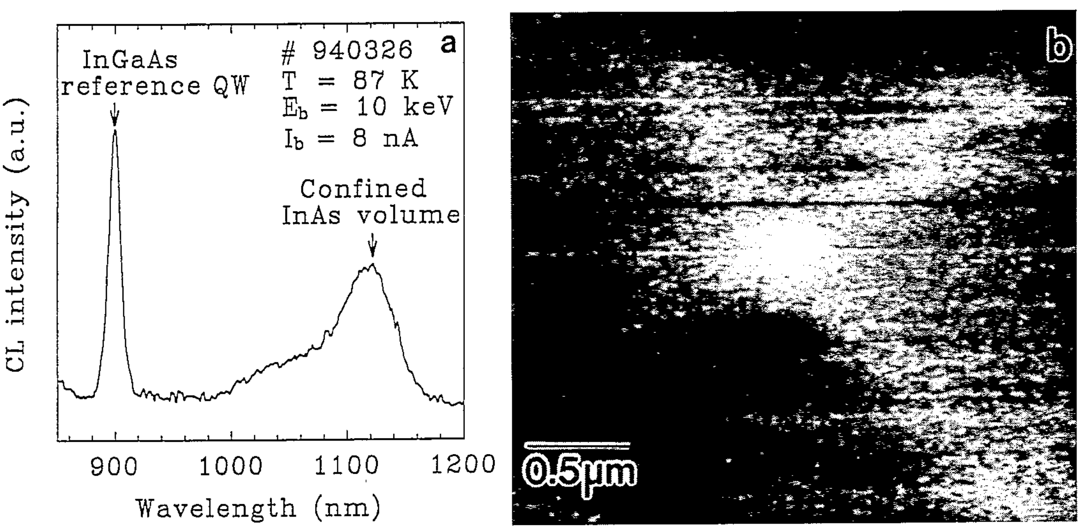

Fig. 4. (a) Area-averaged CL spectra from mesa top region. (b) CL image of mesa taken at 1120 nm emission.

mesa pinch-off. In order to identify the spatial origin of this InAs related peak, simultaneous images using the CL signal at 1120 nm and secondary electron signal from the mesa were acquired. A CL image taken in this fashion is shown in Fig. 4b and reveals that the intense emission at 1120 nm is from a circular region centered on the mesa top.

In summary, we have demonstrated the viability of size-reducing epitaxy on patterned nonplanar (001) semiconductor substrates for realizing *three*-dimensionally confined semiconductor nanostructures of both lattice matched and highly lattice-mismatched semiconductor combinations, provided appropriate pattern orientation following the notions embodied in SESRE is chosen. GaAs and InAs volumes confined in all three dimensions by AlGaAs and GaAs barriers, respectively, have been realized on this surface. Furthermore, for the highly strained InAs on GaAs, use of size-reduced mesas is shown for the first time to result in a dramatic enhancement of the critical thickness for three-dimensional island formation due to strain relief provided by the small mesas.

This work was supported by the ARO, AFOSR, and ONR.

References

[1] S.P. Beaumont and C.V. Sotomayor Torres, Eds., Science and Engineering of One- and Zero-Dimensional Semiconductors (Plenum, New York, 1989);
W. Kirk and M.A. Reed, Eds., Nanostructure and Mesoscopic Systems (Academic Press, New York, 1992).

[2] A. Madhukar, K.C. Rajkumar and P. Chen, Appl. Phys. Lett. 62 (1993) 1547.

[3] K.C. Rajkumar, A. Madhukar, P. Chen, A. Konkar, L. Chen, K. Rammohan and D.H. Rich, J. Vac. Sci. Technol. B 12 (1994) 1071.

[4] For a recent overview of nanostructure formation via growth on nonplanar patterned substrates, see: A. Madhukar, Thin Solid Films 231 (1993) 8.

[5] S. Ando, T. Honda and N. Kobayashi, Jap. J. Appl. Phys. 32 (1993) L104.

[6] M. Lopez, T. Ishiwara and Y. Nomura, Jap. J. Appl. Phys. 32 (1993) L1051.

[7] S. Guha, A. Madhukar and K.C. Rajkumar, Appl. Phys. Lett. 57 (1990) 2110.

[8] J.M. Moison, F. Houzay, F. Barthe, L. Leprince, E. André and O. Vatel, Appl. Phys. Lett. 64 (1994) 196.

[9] A. Madhukar, Q. Xie, P. Chen and A. Konkar, Appl. Phys. Lett. 64 (1994) 2727.

[10] Q. Xie, P. Chen, A. Kalburge, T.R. Ramachandran, A. Nayfonov, A. Konkar and A. Madhukar, J. Crystal Growth 150 (1995) 357.

[11] K.C. Rajkumar, K. Kaviani, J. Chen, P. Chen and A. Madhukar, Appl. Phys. Lett. 60 (1992) 850.

[12] S. Guha, A. Madhukar, Li Chen, K.C. Rajkumar and R.M. Kapre, SPIE Proc. 1285 (1990) 160;
S. Guha, PhD Dissertation, University of Southern California (1991).