phys. stat. sol. (a) **202**, No. 8, R85–R87 (2005) / **DOI** 10.1002/pssa.200510031

pss +++rapid research letters+++
www.pss-rapid.com

Self-assembly of GaAs holed nanostructures by droplet epitaxy

Zhiming M. Wang[*], **Kyland Holmes, John L. Shultz, and Gregory J. Salamo**

Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

Received 5 April 2005, revised 21 April 2005, accepted 9 May 2005
Published online 11 May 2005

PACS 61.46.+w, 68.37.Ps, 68.55.Ac, 81.15.Hi, 81.16.Dn

---

[*] Corresponding author: e-mail zmwang@uark.edu

We report on Ga nano-droplets on GaAs(100) that are not stable under arsenic flux. Spontaneous evolution in shape leads to many interesting GaAs nanostructures. GaAs nanocrystals shaped like lighted candles and square-holed round coins are observed under different growth conditions. The underlying physics of the formation of these interesting nanostructures can be understood in terms of GaAs growth under a uniform arsenic flux and a non-uniform Ga supply from the Ga nano-droplets. These novel shaped GaAs nanostructures, in an AlGaAs matrix, offer promising applications in optoelectronics.

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Semiconductors show dramatic quantization effects when carriers are confined by potential barriers to nano-scale regions of space in one, two, or three dimensions. For example, the optoelectronic properties of semiconductor nanostructures can be modified by structurally engineering the size and shape of nanostructures. Fabrication of active semiconductor nanostructures, however, is extremely challenging due to technology limitations at these dimensions. Self-assembly of semiconductor nanostructures, however, provides a rich spectrum of opportunity. The most common approach to the self-assembly of nanostructures has been the Stranski–Krastanow (SK) method. In the SK approach to the formation of nanostructures, a thin semiconductor film is deposited onto a different semiconductor substrate that presents a high mismatch in lattice constant between the substrate and the thin film material being deposited [1, 2]. The lattice mismatch then self-assembles quantum dots or quantum wires having relatively simple geometries [1–6]. Even more complicated configurations are possible, however, such as quantum rings and quantum dot chains [7–10] which are currently drawing much attention. Compared to colloidal nanocrystals, which have been observed to be rod-, arrow-, teardrop- and tetrapod-shaped [11], the shapes of the semiconductor nanostructures fabricated by epitaxy at first seem less attractive. Yet, epitaxial nanostructures with more interesting shapes will likely have novel optical and electrical properties based on the effects of shape.

While the SK growth approach has had dramatic success with lattice-mismatched systems a different approach is needed for lattice matched systems, such as GaAs/AlGaAs. Lattice matched material systems can have as much, if not more, technological importance. Although not studied with as much fever, droplet epitaxy offers the possibility of formation of quantum dots without the need for a lattice mismatch. In droplet epitaxy of GaAs/AlGaAs, Ga is first deposited to create liquid Ga droplets on an AlGaAs surface and subsequently exposured to a high arsenic flux that transforms the droplets into GaAs nano-crystals [12, 13]. In this letter, we extend the capability of droplet epitaxy to the growth of more interesting GaAs nanostructure geometrical shapes never explored before. GaAs lighted nano-candles and square-holed round nano-coins are observed under different growth conditions.

2 Experimental All the samples investigated here were grown on epi-ready GaAs(100) substrates by molecular beam epitaxy (MBE) which is equipped with a reflection high-energy electron diffraction (RHEED) system and a highly accurate (±2 °C) optical transmission thermometry system for substrate temperature determination. A valve-controlled As source was used, which enables instantaneous changes in the As flux depending on the valve position. Following the growth of about 300 nm of a GaAs buffer layer at 600 °C, an $Al_{0.3}Ga_{0.7}As$ layer of 200 monolayers (MLs) was deposited to be a barrier for the further growth

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

of GaAs nanostructures. Subsequently, the substrate was cooled to 380 °C. The As-valve was fully closed before reaching the desired substrate temperature. Once the growth temperature was reached, Ga atoms were supplied to form Ga droplets on the $Al_{0.3}Ga_{0.7}As$ surface, corresponding to the amount necessary for the growth of 10.5 ML of GaAs. The sample was then annealed for 45 s under As-flux with As-valve fully or 10% opened. The achieved morphology was quenched and ambient measurements of atomic force microscopy (AFM) were carried out on the samples taken out from the MBE chamber.

3 Results and discussion

Figures 1(a) and (b) are AFM images of the sample with the subsequent annealing carried out with the As-valve fully opened. The observed density of GaAs nanostructures is about 14 μm^{-2}. The nanostructures obtained look like a lighted candle in shape. In this analogy, the flame, the highest part of the GaAs nanostructures, points in the [011] direction, rising up about 10 nm from the ring-like base (top of the candle). Meanwhile, this base is about 15 nm in height above the background and about 90 nm in diameter.

On the other hand, when the sample with Ga droplets formed at 380 °C was annealed under 10% opened As source, nice ring-like GaAs nanostructures were observed as shown in the AFM image of Fig. 2(a). A zoom-in AFM image in Fig. 2(b) shows that the outer perimeter is actually more round than the inner perimeter. The formed nanostructure looks like an ancient Chinese coin – round with a square hole. The deepest trench in the square hole can be over 2.8 nm under the base plane. The ring-like feature rises up from the base about 2 nm.

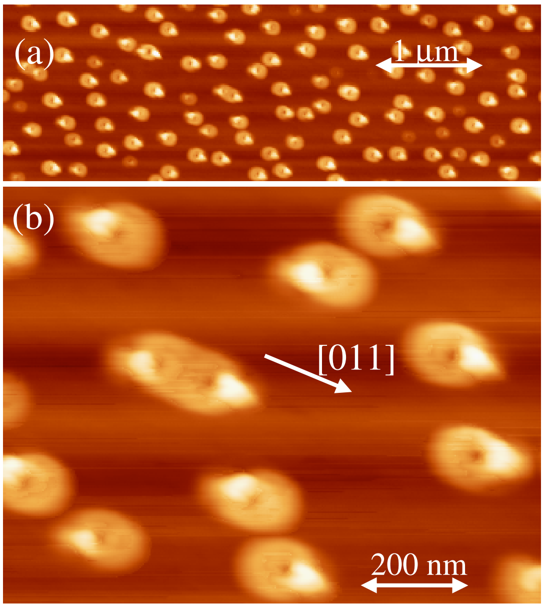

Figure 1 (online colour at: www.pss-rapid.com) AFM images at different magnification showing the shape of GaAs nanostructures formed through arsenization of Ga droplets with a fully opened As-valve.

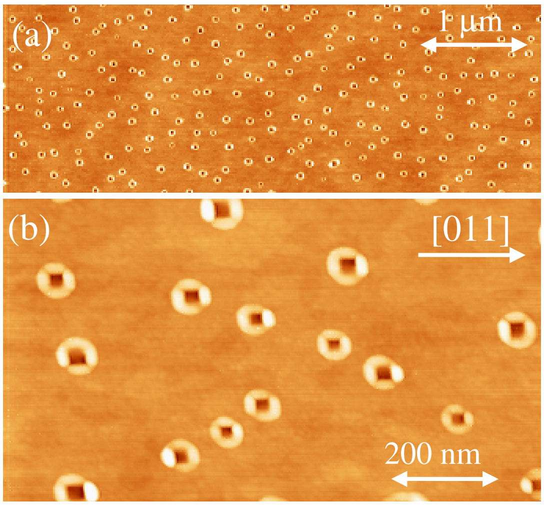

Figure 2 (online colour at: www.pss-rapid.com) AFM images at different magnification showing the shape of GaAs nanostructures formed through arsenization of Ga droplets with a 10% opened As-valve.

The observed general features of the GaAs nanostructures can be understood qualitatively, in terms of GaAs growth with a uniform As-flux but a non-uniform Ga supply (from Ga droplets). In principle, the growth of GaAs on an $Al_{0.3}Ga_{0.7}As$ surface will proceed in a layer-by-layer fashion. The Ga droplets are unstable under an As flux and the Ga is transported down the droplet. When the uniform As-flux is low (10% opened), the Ga supply from the droplets provides a Ga-rich condition. In fact, an As-limited layer-by-layer growth was evidenced by the observation of RHEED oscillations. We actually used the oscillations to determine the As-flux. The As source with the valve at 10% opened provide enough arsenic flux for a GaAs growth rate of 0.33 ML/s. The 45 second annealing period is more than enough to fully crystallize the 10.5 ML Ga droplets into GaAs nanostructures. Similar methods for the determination of As-flux have been used two decades ago [14, 15] but for the first time we use this method to fabricate interestingly shaped GaAs nanostructures. The lower As-flux enhances two-dimensional growth, or in other words, enhances the down-hill material transportation from the Ga droplets. Therefore, the GaAs nanostructures observed with fully opened As-valve are taller than those with 10% opened As-valve.

All of the interesting nanostructures observed in this investigation have a concave center. In the phase diagram of the Ga–As system, Ga, As and GaAs are the only stable phases [16]. For this reason, the As cannot penetrate the Ga droplet. As a result it can at best form GaAs at the droplet surface. However, this interface energy is high (as evidenced by the formation of the Ga droplet on a GaAs surface) and the GaAs growth at the surface is transported to the lower energy region around the droplet. In other words, the GaAs growth can only proceed around the droplet by a self-limited Ga down-hill transportation and a uniform As-flux, as illustrated in Fig. 3 from (a) to (b). In

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

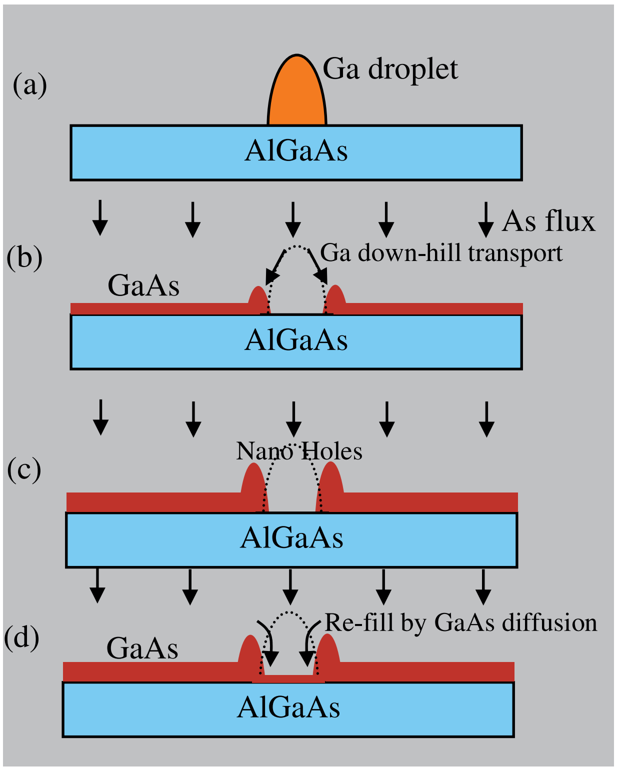

Figure 3 (online colour at: www.pss-rapid.com) Schematic illustration of progressive stages for the formation of holed nanostructures during droplet epitaxy.

principle, the center of the Ga droplet should have no GaAs growth until all the Ga material in droplets run out, as shown in Fig. 3(c). This means the concave center can be as deep as 10.5 ML, or 3.0 nm. The trench deeper than 2.8 nm observed in Fig. 2 is consistent with the above discussion. The deep center will be gradually refilled by GaAs diffusion after all Ga has been converted into GaAs as shown in Fig. 3(d). While the base of initial Ga droplets is round, the observed holes are square-like due to the dependence of Ga migration on surface orientation. The concave center of GaAs nanostructures formed by droplet epitaxy has been reported before [12, 13], but not deep into the base plane as we observed here. Our observation may provide a useful route to grow nano holes for further quantum structure engineering [17].

InGaAs quantum rings, one type of holed nanostructures, has been observed, where liquid InAs is believed to be present as the result of biaxial stress [8]. While the instability of InAs islands is induced by the deposition of GaAs for the formation of InGaAs quantum rings [7, 8], the origin of GaAs holed nanostructures here is the instability of Ga droplets under arsenic flux.

It is interesting to note that the ML-high islands on about 10.5 ML GaAs quantum wells have been extensively studied as natural quantum dots [18]. By using droplet epitaxy, the natural corrugation can be controlled very efficiently. We have studied the stability of the strange nanostructures annealed at higher temperature and found the structures are stable at least up to 500 °C. Therefore, the holed nanostructures may find applications after they are buried with an AlGaAs layer, creating quantum confinement. The high quality of buried nanostructures in optical properties has been indicated by photoluminescence from quantum dots formed by droplet epitaxy [12, 13]. Direct optical investigations on the nanostructures observed here will be addressed in future publications.

4 Conclusion

GaAs nano-crystals shaped like lighted candles and square-holed round coins have been observed on an $Al_{0.3}Ga_{0.7}As$ surface during droplet epitaxy. The observation of interesting GaAs nano-crystals may excite more research efforts on utilizing the droplet epitaxy technique to fabricate specific nanostructures for other lattice-matched and lattice-mismatched systems. For the evolution of GaAs nanostructures on the $Al_{0.3}Ga_{0.7}As$ surface, the nature of droplet epitaxy was revealed as GaAs growth generated from a non-uniform Ga supply from nanodroplets and a uniform As-flux.

References

[1] D. Bimberg, M. Grundmann, and N. N. Ledentsov, Quantum Dot Heterostructures (Wiley, Chichester, 1999).
[2] P. M. Petroff, A. Lorke, and A. Imamoglu, Phys. Today **54**, 46 (2001).
[3] D. Leonard, M. Krishnamurthy, C. M. Reaves, S. P. DenBaars, and P. M. Petroff, Appl. Phys. Lett. **63**, 3203 (1993).
[4] Q. Xie, A. Madhukar, P. Chen, and N. P. Kobayashi, Phys. Rev. Lett. **75**, 2542 (1995).
[5] Zh. M. Wang, Sh. Seydmohamadi, J. H. Lee, and G. J. Salamo, Appl. Phys. Lett. **85**, 5031 (2004).
[6] H. Wen, Z. M. Wang, and G. J. Salamo, Appl. Phys. Lett. **84**, 1756 (2004).
[7] R. J. Warburton, B. Urbaszek, E. J. McGhee, C. Schulhauser, A. Högele, K. Karrai, A. O. Govorov, J. M. Garcia, B. D. Gerardot, and P. M. Petroff, Nature **427**, 135 (2004).
[8] D. Granados and J. M. Garcia, Appl. Phys. Lett. **82**, 2401 (2003).
[9] S. S. Li and J. B. Xia, J. Appl. Phys. **89**, 3434 (2001).
[10] Z. M. Wang, K. Holmes, Yu. I. Mazur, and G. J. Salamo, Appl. Phys. Lett. **84**, 1931 (2004).
[11] L. Manna, E. C. Scher, and A. P. Alivisatos, J. Am. Chem. Soc. **122**, 12700 (2000).
[12] C. D. Lee, C. Park, H. J. Lee, K. S. Lee, S. J. Park, C. G. Park, S. K. Noh, and N. Koguchi, Jpn. J. Appl. Phys. **37**, 7158 (1998).
[13] K. Watanabe, N. Koguchi, and Y. Gotoh, Jpn. J. Appl. Phys. **39**, L79 (2000).
[14] J. H. Neave, B. A. Joyce, and P. J. Dobson, Appl. Phys. A **34**, 79 (1984).
[15] B. F. Lewis, R. Fernandez, A. Madhukar, and F. J. Grunthaner, J. Vac. Sci. Technol. B **4**, 560 (1986).
[16] Landolt-Börnstein, New Series IV/5a (Springer, Berlin, 1991), p. 297.
[17] A. Rastelli, S. Stufler, A. Schliwa, R. Songmuang, C. Manzano, G. Costantini, K. Kern, A. Zrenner, D. Bimberg, and O. G. Schmidt, Phys. Rev. Lett. **92**, 166104 (2004).
[18] D. Gammon, E. S. Snow, B. V. Shanabrook, D. S. Katzer, and D. Park, Phys. Rev. Lett. **76**, 3005 (1996).

© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim