St. Petersburg Polytechnic University Journal. Physics and Mathematics. 2023. Vol. 16. No. 3.1
Научно-технические ведомости СПбГПУ. Физико-математические науки. 16 (3.1) 2023

Conference materials
UDC 538.9.
DOI: https://doi.org/10.18721/JPM.163.109

Formation of symmetrical nanoholes by local droplet etching for site-controlled growth of single quantum dots

E.A. Lakhina ✉, N.A. Shandyba, N.E. Chernenko,
D.V. Kirichenko, S.V. Balakirev, M.S. Solodovnik

Southern Federal University, Taganrog, Russia
✉ lakhina@sfedu.ru

Abstract. In this paper, we study local etching of the GaAs(001) surface by Ga droplets at various technological conditions. Effects of the deposition temperature and thickness, interruption time, annealing temperature and arsenic background pressure are discussed. A minimum deposition thickness of 1.5 monolayer of Ga is found to be sufficient to etch the GaAs surface. We demonstrate that an increase in the annealing temperature leads to a decrease in the hole depth and an increase in their diameter. For the first time, we obtain symmetrical nanoholes of pyramidal shape on the GaAs(001) surface with a low surface density (~ $1 \cdot 10^8$ cm^{-2} and below) allowing subsequent formation of single quantum dots for high-efficiency quantum photonic devices.

Keywords: epitaxy, local droplet etching, gallium arsenide, A3B5

Funding: This study was funded by the Russian Science Foundation Grant No. 22-79-10251, https://rscf.ru/project/22-79-10251/, at the Southern Federal University.

Citation: Lakhina E.A., Shandyba N.A., Chernenko N.E., Kirichenko D.V., Balakirev S.V., Solodovnik M.S., Formation of symmetrical nanoholes by local droplet etching for site-controlled growth of single quantum dots, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 53–58. DOI: https://doi.org/10.18721/JPM.163.109

Материалы конференции
УДК 538.9.
DOI: https://doi.org/10.18721/JPM.163.109

Формирование симметричных наноуглублений методом локального капельного травления для позиционированного роста одиночных квантовых точек

Е.А. Лахина ✉, Н.А. Шандыба, Н.Е. Черненко,
Д.В. Кириченко, С.В. Балакирев, М.С. Солодовник

Южный федеральный университет, г. Таганрог, Россия
✉ lakhina@sfedu.ru

Аннотация. В работе представлены результаты экспериментальных исследований процессов локального травления поверхности GaAs(001) каплями Ga при различных технологических режимах. Впервые на поверхности GaAs с ориентацией (001) получены симметричные наноуглубления пирамидальной формы с низкой поверхностной плотностью (~ $1 \cdot 10^8$ см$^{-2}$ и ниже), позволяющие обеспечить дальнейшее формирование в них одиночных квантовых точек для высокоэффективных устройств квантовой фотоники.

Ключевые слова: эпитаксия, локальное капельное травление, арсенид галлия, A3B5

Финансирование: Исследование выполнено за счет гранта Российского научного фонда № 22-79-10251, https://rscf.ru/project/22-79-10251/, в Южном федеральном университете.

Ссылка при цитировании: Лахина Е.А., Шандыба Н.А., Черненко Н.Е., Кириченко Д.В., Балакирев С.В., Солодовник М.С., Формирование симметричных наноуглублений методом локального капельного травления для позиционированного роста одиночных квантовых точек // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 53–58. DOI: https://doi.org/10.18721/JPM.163.109

Introduction

Epitaxially grown single quantum dots (QDs) are among the main candidates for use as sources of single and entangled photons due to their ability to generate photons on demand with high extraction efficiency [1] and near-unity indistinguishability [2], as well as due to the versatility of their device manufacturing technology [3]. One of the problems in creating high-quality QD-based polarization-entangled photon sources is that the time-dependent phase factor of the two-photon state induced by exciton fine structure splitting (FSS) can significantly affect a degree of similarity of a real entangled photon pair with the ideal Bell pair (entanglement fidelity) [4]. Obtaining a high entanglement fidelity requires the in-plane confinement potential symmetry of an epitaxial QD to eliminate FSS [5]. To fulfil this requirement, parameters of QD arrays with high structural symmetry must be precisely controlled. For example, QD elongation and stress inhomogeneity are often caused by anisotropy of atom migration and interdiffusion during In(Ga)As/GaAs QD growth by a widely used Stranski-Krastanov method [6].

To date, there are several ways to form highly efficient symmetric QDs, including InGaAs QDs in inverted pyramidal cavities obtained by liquid etching [7], InAsP QDs in InP nanowires [8], (In)GaAs QDs formed by high-temperature droplet epitaxy or grown on high-index surfaces [9], etc. One more advantageous method of the formation of GaAs/AlGaAs QDs is so-called local droplet etching (LDE) [10] involving two main stages. The first stage consists in the formation of group III metal (Ga, In, Al) droplets on the epitaxial surface in the absence of arsenic vapor by the Folmer-Weber mechanism. The second stage is the subsequent etching of the surface under the influence of elevated temperature and a small arsenic flux [11]. LDE allows formation of ultra-low density QDs without any lithography and can be easily integrated into the process of growing heterostructures by molecular beam epitaxy. Compared to other listed techniques, LDE-based QDs demonstrate the best characteristics of non-classical light emission so far. Recent studies have presented unprecedented high levels of photon pair entanglement and indistinguishability [12], as well as teleportation [13] and entanglement swapping [14] generated in GaAs/AlGaAs nanostructures fabricated by LDE. The development of the LDE method in recent years has significantly improved the understanding of the mechanisms of droplet formation and subsequent etching of the underlying surface. LDE allows formation of hole arrays with various parameters, including ultra-low density, allowing one to further obtain an array of isolated single QDs [15]. However, as analysis of the literature data shows, there are still no reports on the LDE formation of low-density symmetric nanoholes with pyramidal faceting on technologically important GaAs surfaces with (001) orientation. These holes must be distinguished by a unit ratio of longitudinal diameter to transverse diameter and a large depth, allowing a good localization of QDs in them.

The purpose of this work is an experimental study of technological conditions of Ga/GaAs(001) droplet etching which make it possible to obtain symmetrical pyramidal-shaped nanoholes with a density of about $1 \cdot 10^8$ cm^{-2} and below. To achieve this goal, it is necessary to consider numerous parameters affecting the mechanisms of droplet formation and subsequent surface etching: substrate temperature, amount of deposited material, temperature and time of the sample annealing, arsenic vapor pressure, etc.

Materials and Methods

Experimental studies were carried out on epi-ready GaAs(001) substrates using SemiTEq STE35 molecular beam epitaxy equipment. Knudsen effusion cells were used as sources of group-III species and a valved cracker cell was used as a source of arsenic.

After a standard procedure of oxide removal and subsequent growth of 250-nm-thick GaAs buffer layer, the arsenic source was closed to provide a low background pressure in the chamber (from $1.5 \cdot 10^{-7}$ Pa to $3.5 \cdot 10^{-7}$ Pa). Then, Ga atoms were deposited on the surface in the amount of 1.1, 1.5, 2 and 5 equivalent monolayers (ML) at a substrate temperature of 500 °C. At the next stage, the substrate was annealed to 550 °C, 580 °C, and 610 °C for 15, 30 and 45 minutes. After the annealing, samples were cooled down and unloaded from the chamber for characterization in atomic force (AFM) and scanning electron microscopes (SEM).

Results and Discussion

AFM images of hole arrays obtained after etching by droplets formed at various deposition amounts of Ga at a temperature of 500 °C are shown in Fig. 1. An analysis of the results obtained indicates that 1.1 ML Ga is not enough to obtain droplets capable of etching deep nanoscale regions of the surface (Fig. 1, *a*). At the same time, in other cases, there are arrays of holes with different average diameters which increase as the amount of deposited material increases. The surface density of holes for the indicated samples is $3 \cdot 10^{-7}$ cm^{-2} (1.5 ML, not shown), $9 \cdot 10^{-7}$ cm^{-2} (2 ML, Fig. 1, *b*) and $1 \cdot 10^{-8}$ cm^{-2} (5 ML, Fig. 1, *c*). This range of the surface densities satisfies the requirement that the average distance between holes is about 1 μm or more. The difference in the surface density of holes may be associated with random fluctuations of the substrate temperature during local droplet etching. The depth of the formed holes increases from 1.6 nm for a sample with a deposition thickness of 2.0 ML Ga to 5.3 nm for 5 ML Ga (Fig. 1, *b*, *c*), which is associated with an increase in the droplet volume. Droplets in this case are the source of atoms displacing the underlying material in the etching process [16].

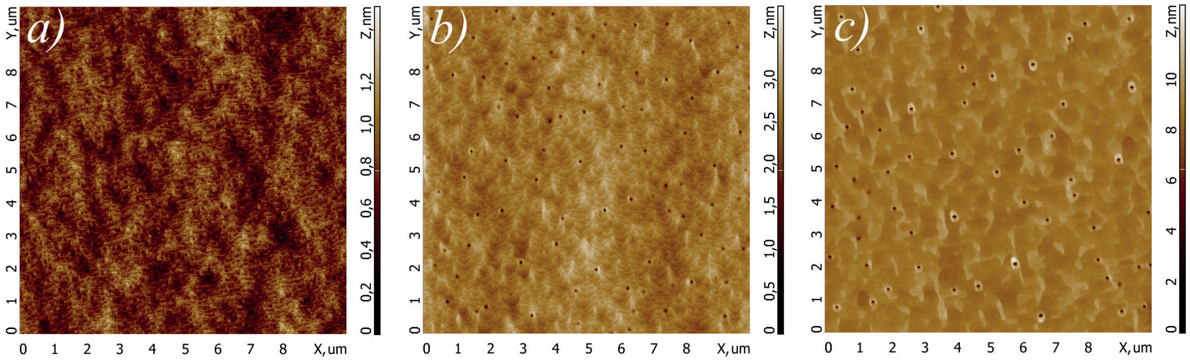

Fig. 1. AFM images of the GaAs surface after etching by droplets formed at various amounts of deposited Ga: 1.1 ML (*a*), 2.0 ML (*b*) and 5.0 ML (*c*)

As was shown in previous studies [17], holes must be sufficiently deep to increase the probability of island nucleation within them and, consequently, to increase selectivity of subsequent QD growth. In this regard, a value of 5 ML was chosen as the preferred amount of deposited Ga material for further studies.

At the next stage, the interruption time between the stages of droplet deposition and subsequent substrate heating to an annealing temperature was considered. It was found that an increase in the interruption time from 1 to 15 minutes reduces the root-mean-square deviation of the average hole diameter from 12 to 5% (Fig. 2 *a*, *b*), which is associated with redistribution of the material during Ostwald ripening [18] and increasing the homogeneity of the droplets immediately before etching.

An influence of the annealing temperature on the hole characteristic was also studied. It was found that an increase in the annealing temperature from 580 °C (Fig. 2, *b*) to 610 °C (Fig. 2, *c*) leads to a decrease in the average hole depth from 4.3 to 1.0 nm and an increase in their average diameter from 103 to 159 nm. A typical rim formed as a result of droplet crystallization in the

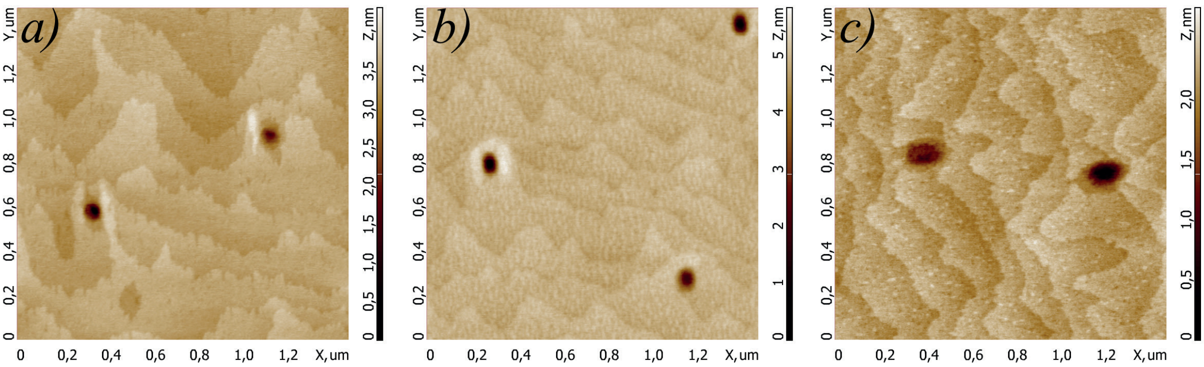

Fig. 2. AFM images of the GaAs surface after etching by droplets formed after various interruption times and annealing temperatures: 1 min, 580 °C (*a*), 15 min, 580 °C (*b*) and 15 min, 610 °C (*c*)

arsenic flux at the boundary of the triple point (Fig. 2, *a*, *b*) is removed when the annealing temperature is increased up to $T = 610$ °C (Fig. 2, *c*). However, a decrease in the depth and an increase in the hole diameter reduce the attractiveness of using holes annealed at $T = 610$ °C due to a decrease in the probability of island nucleation in them or the potential initiation of polycentric nucleation observed in holes with a large diameter [17].

Symmetrical pyramidal holes with the required surface density were obtained by reducing the background pressure of arsenic to a value of $1.5\cdot10^{-7}$ Pa at an annealing temperature of 550 °C and a different annealing time from 15 to 45 minutes (Fig. 3). Annealing during 15 minutes leads to the formation of deep faceted holes in the center of thin pedestals (Fig. 3, *a*) which have an elongated shape because of anisotropy of the surface diffusion of adatoms. 15 additional minutes of annealing does not change the surface morphology significantly, but some of pedestals disappear reducing the depth of holes (Fig. 3, *b*). Long annealing during 45 minutes leads to the elimination of pedestals around almost all holes (Fig. 3, *c*). Although deep holes remain pyramidal in this case, their fraction is much smaller than at shorter annealing times.

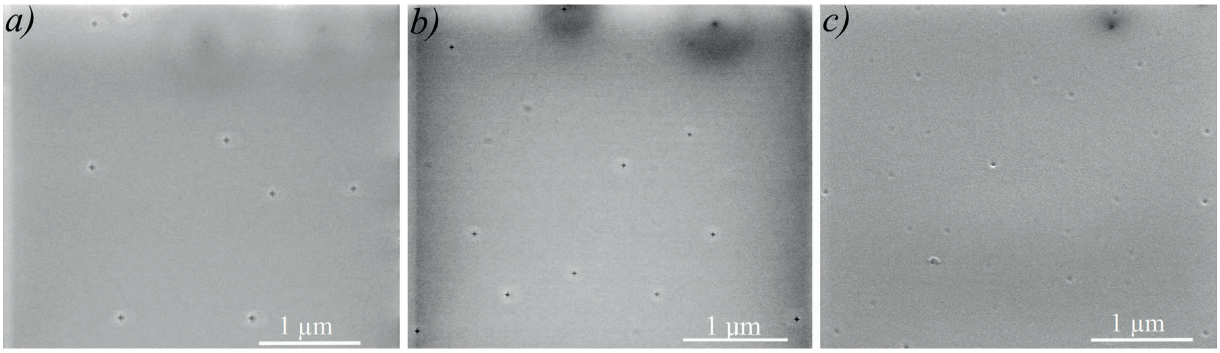

Fig. 3. SEM images of the GaAs surface after etching by droplets at 550 °C during various annealing intervals: 15 min (*a*), 30 min (*b*) and 45 min (*c*)

Fig. 4 shows AFM image of surface obtained after droplet etching at an arsenic pressure of $1.5\ 10^{-7}$ Pa (Fig. 4, *a*) and AFM cross-section of a typical nanohole for two mutually perpendicular directions (Fig. 4, *b*).

As presented in Fig. 4, *b*, the characteristic hole for the obtained samples has lateral walls in the form of flat faces and the same shape and size in different lateral directions. A pedestal around the hole has a height of about 2 nm and a near-circular elongated shape. According to the AFM cross-section (Fig. 4, *b*), the hole depth reaches 15 nm, which is expected to benefit further localization of epitaxial nanostructures within predefined nucleation centers [17].

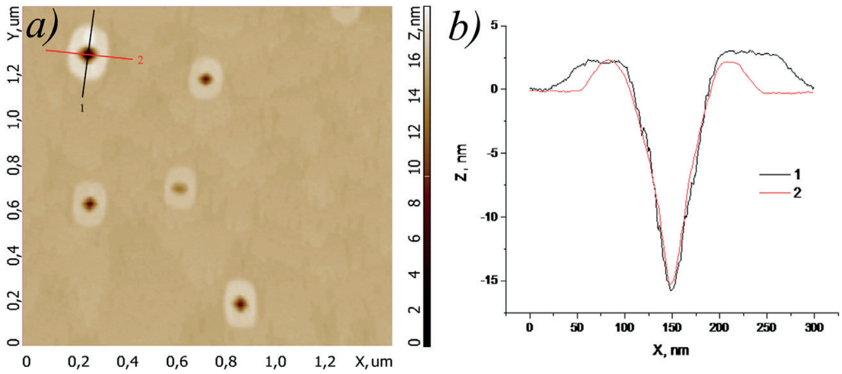

Fig. 4. AFM image of the GaAs surface after droplet etching at an arsenic pressure of $1.5 \cdot 10^{-7}$ Pa (*a*) and AFM cross-section of a typical hole shown in Fig. 4, *a* (*b*).

Conclusion

Thus, pyramidal nanoholes for the subsequent localization of highly symmetrical QDs in them can be obtained on the GaAs(001) surface by local etching with Ga droplets at a low background arsenic pressure ($1.5 \cdot 10^{-7}$ Pa) and annealing temperature of 550 °C.

REFERENCES

1. **Vajner D. A., Rickert L., Gao T., Kaymazlar K., Heindel T.,** Communication Using Semiconductor Quantum Dots, Advanced Quantum Technologies. 5 (7) (2022) 2100116.

2. **Da Lio B., Faurby C., Zhou X., Chan M.L., Uppu R., Thyrrestrup H., Scholz S., Wieck A.D., Ludwig A., Lodahl P., Midolo L.,** A Pure and Indistinguishable Single-Photon Source at Telecommunication Wavelength, Advanced Quantum Technologies. 5 (5) (2022) 2200006.

3. **Tonndorf P., Del Pozo-Zamudio O., Gruhler N., Kern J., Schmidt R., Dmitriev A.I., Bakhtinov A.P., Tartakovskii A.I., Pernice W.,** Michaelis de Vasconcellos S., Bratschitsch R., On-Chip Waveguide Coupling of a Layered Semiconductor Single-Photon Source, Nano Letters. 17 (9) (2017) 5446–5451.

4. **Singh R., Bester G.,** Nanowire quantum dots as an ideal source of entangled photon pairs, Physical Review Letters. 103 (6) (2009) 63601.

5. **Juska G., Dimastrodonato V., Mereni L. O., Gocalinska A., Pelucchi E.,** Towards quantum-dot arrays of entangled photon emitters, Nature Photonics. 7 (7) (2013) 527–531.

6. **Luo J.-W., Singh R., Zunger A., Bester G.,** Influence of the atomic-scale structure on the exciton fine-structure splitting in InGaAs and GaAs quantum dots in a vertical electric field, Physical Review B. 86 (16) (2012) 161302.

7. **Chung T.H., Juska G., Moroni S. T., Pescaglini A., Gocalinska A., Pelucchi E.,** Selective carrier injection into patterned arrays of pyramidal quantum dots for entangled photon light-emitting diodes, Nature Photonics. 10 (12) (2016) 782–787.

8. **Versteegh M.A.M., Reimer M.E., Jцns K.D., Dalacu D., Poole P.J., Gulinatti A., Giudice A., Zwiller V.,** Observation of strongly entangled photon pairs from a nanowire quantum dot, Nature Communications. 5 (2014) 5298.

9. **Basso Basset F., Bietti S., Reindl M., Esposito L., Fedorov A., Huber D., Rastelli A., Bonera E., Trotta R., Sanguinetti S.,** High-Yield Fabrication of Entangled Photon Emitters for Hybrid Quantum Networking Using High-Temperature Droplet Epitaxy, Nano Letters. 18 (1) (2018) 505–512.

10. **Huo Y.H., Křápek V., Rastelli A., Schmidt O.G.,** Volume dependence of excitonic fine structure splitting in geometrically similar quantum dots, Physical Review B. 90 (4) (2014) 041304.

11. **Heyn C., Bartsch T., Sanguinetti S., Jesson D., Hansen W.,** Dynamics of mass transport during nanohole drilling by local droplet etching, Nanoscale Research Letters. 10 (1) (2015) 1–9.

12. **Liu J., Su R., Wei Y., Yao B., Silva S.F.C. da, Yu Y., Iles-Smith J., Srinivasan K., Rastelli A., Li J., Wang X.,** A solid-state source of strongly entangled photon pairs with high brightness and indistinguishability, Nature Nanotechnology. 14 (6) (2019) 586–593.

13. **Reindl M., Huber D., Schimpf C., Covre da Silva S.F., Rota M.B., Huang H., Zwiller V., Jöns K.D., Rastelli A., Trotta R., da Silva S. F. C., Rota M. B., Huang H., Zwiller V., Jцns K.D., Rastelli A., Trotta R.,** All-photonic quantum teleportation using on-demand solid-state quantum emitters, Science Advances. 4 (12) (2018) 1–8.

14. **Zopf M., Keil R., Chen Y., Yang J., Chen D., Ding F., Schmidt O.G.,** Entanglement Swapping with Semiconductor-Generated Photons Violates Bell's Inequality, Physical Review Letters. 123 (16) (2019) 160502.

15. **Heyn C., Feddersen S.,** Modeling of Al and Ga droplet nucleation during droplet epitaxy or droplet etching, Nanomaterials. 11 (2) (2021) 1–13.

16. **Heyn C., Stemmann A., Klingbeil M., Strelow C., Köppen T., Mendach S., Hansen W.,** Mechanism and applications of local droplet etching, Journal of Crystal Growth. 323 (1) (2011) 263–266.

17. **Heyn C., Zocher M., Pudewill L., Runge H., Küster A., Hansen W.,** Droplet etched GaAs quantum dots close to surfaces and metallic interfaces, Journal of Applied Physics. 121 (4) (2017) 044306.

18. **Ostwald W.,** Lehrbuch der Allgemeinen Chemie, Leipzig, Germany. (Vol. 2) (1896).

THE AUTHORS

LAKHINA Ekaterina A.
lakhina@sfedu.ru
ORCID: 0000-0002-9326-2418

SHANDYBA Nikita A.
shandyba@sfedu.ru
ORCID: 0000-0001-8488-9932

CHERNENKO Natalia E.
nchernenko@sfedu.ru
ORCID: 0000-0001-8468-7425

KIRICHENKO Danil V.
dankir@sfedu.ru
ORCID: 0000-0001-7476-2778

BALAKIREV Sergey V.
sbalakirev@sfedu.ru
ORCID: 0000-0003-2566-7840

SOLODOVNIK Maxim S.
solodovnikms@sfedu.ru
ORCID: 0000-0002-0557-5909

Received 14.07.2023. Approved after reviewing 05.09.2023. Accepted 07.09.2023.