Semiconductors, 2023, Vol. 57, No. 8

Selective area epitaxy of InP/GaInP$_2$ quantum dots from metal-organic compounds

© *A.S. Vlasov*[1], *K.M. Afanasev*[1], *A.I. Galimov*[1], *N.A. Kalyuzhnyy*[1], *D.V. Lebedev*[1],
A.V. Malevskaya[1], *S.A. Mintairov*[1], *M.V. Rakhlin*[1], *R.A. Salii*[1],
A.M. Mozharov[2], *I.S. Mukhin*[2], *A.M. Mintairov*[1,3]

[1] Ioffe Institute,
194021 St. Petersburg, Russia
[2] Alferov University, Russian Academy of Sciences,
194021 St. Petersburg, Russia
[3] University of Notre Dame, Notre Dame,
Indiana, USA 46556

E-mail: vlasov@scell.ioffe.ru

Received May 11, 2023
Revised July 21, 2023
Accepted October 30, 2023

Experiments on the growth of self-assembled InP/GaInP$_2$ quantum dots in dielectric mask $0.1-1\,\mu$m apertures by MOVPE epitaxy have been carried out. A sequence of operations for the implementation of the lift-off lithography method is proposed and implemented. The possibility of obtaining apertures with 100 nm diameter and less is shown. Combination of thermally deposited SiO$_2$ and wet etching is shown to produce minimal amount of nonradiative defects and results in a stable PL signal from single QDs in the aperture.

Keywords: InP quantum dots, selective area epitaxy, MOVPE epitaxy.

DOI: 10.61011/SC.2023.08.57610.5049C

1. Introduction

Selective area epitaxy (SAE) is one of the promising approaches to creating semiconductor nanostructures and devices based on integrated circuits [1,2]. The SAE method is used both for the growth of nanostructures based on III-V compounds and for the creation of hybrid structures based on silicon. In particular, the method has become quite widespread for the catalytic growth of filamentary nanostructures, since it allows to control their location on the substrate [3,4].

The basis of selective epitaxy is a surface covered with a mask of a neutral material. The main requirements to the material protecting the surface are: the absence of chemical bonds with semiconductor atoms to avoid parasitic growth on the surface of the mask, and temperature stability, which preserves the properties of the mask material during the growth process. As a rule, to create a mask, SiN$_x$, SiO$_2$ and Al$_2$O$_3$ films are used, the apertures in which are prepared by direct lithography with etching of the applied dielectric layer. Selective growth occurs through a dielectric mask. This work is aimed at studying the SAE approach for obtaining quantum dots (QD) in the GaInP$_2$/InP system using metal-organic vapor phase epitaxy (MOVPE). These QD form a type I or II heterojunction with GaInP$_2$, depending on the degree of ordering of the latter, with the main band break in the conduction band, which leads to the fact that only electrons are localized in the QD. One of the potential applications of these QDs is to study the behavior of Wigner molecules generated when several electrons accumulate in a dot, which in turn can be used to build a quantum computer [5].

2. Experiment

Epitaxial growth was carried out on MOVPE epitaxy unit AIX-200/4 (Aixtron, Germany). At the preparation stage, an Ga$_{0.51}$In$_{0.49}$P (abbreviated GaInP$_2$) layer with a thickness of 500 nm was grown on the surface of the epi-ready GaAs substrate (*n*-type, 6^0 off). The surface of the semiconductor was immediately covered with a layer of dielectric to prevent the formation of a natural oxide layer. After the formation of the mask, QD growth was carried out at a temperature of 600°C and the In(CH$_3$)$_3$) flow reduced to $\sim 1/8$ compared to planar QD growth. The decrease in the flux In(CH$_3$)$_3$ indicates a significant influence of horizontal transport on the growth rate when using the SAE method. Due to the fact that the surface recombination rate of InP is relatively low, samples without a capping layer were used for photoluminescence studies.

To deposit a dielectric layer with a thickness of ~ 100 nm, the methods of thermal deposition with heating by an electron beam (SiO$_2$) and plasma-chemical deposition (SiO$_2$, TiO$_2$ and SiN$_x$) were used. Selective etching of the dielectric (SiO$_2$) was carried out through a resist mask using a diluted buffer etchant (BOE — HF : NH$_4$F : H$_2$O) in the proportion 1 : 6 : 320.

Photoluminescence (PL) spectra of QD in apertures were studied using a high spatial resolution setup equipped with an objective lens with magnification 50×. For excitation,

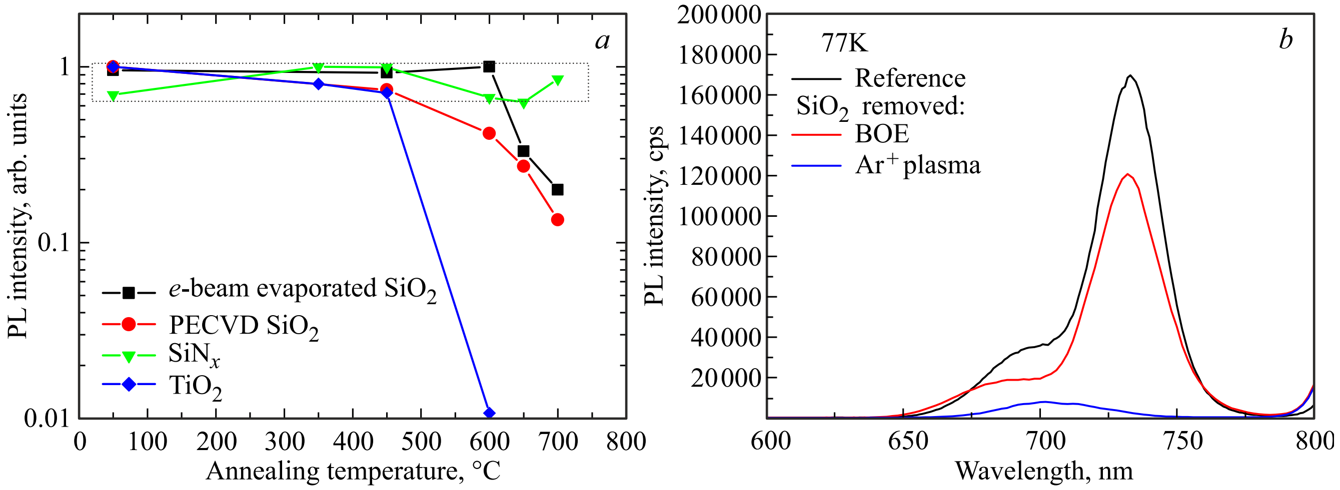

Figure 1. Dependence of the PL intensity $GaInP_2$-InP QD on the annealing temperature for different dielectric materials (*a*) and an example of the PL spectra of QD after removing the SiO_2 layer (*b*).

continuous laser radiation with a wavelength of 532 nm and a power density of $\sim 120\,W/cm^2$ was used. Studies of the influence of dielectric coatings and methods for their removal were carried out on planar samples without lithography. The PL spectra of such samples were measured in a cryostat cooled with liquid nitrogen at a laser radiation power density of $\sim 10\,W/cm^2$. Photographs of the surface of the studied structures were obtained using a Zeiss Neon 40 ESM scanning-electron microscope.

3. Results and discussion

The epitaxy temperature of phosphide compounds III-P is $\sim$ 600–700°C; accordingly, the most important parameter is the temperature stability of the dielectric and its interaction with the $GaInP_2$ layer. To study this parameter, layers of SiN_x, TiO_2 and SiO_2(100 nm) were deposited on the surface of $GaInP_2$, after which the samples were annealed at different temperatures. Before 400°C, annealing was carried out in a stream H_2, at higher temperatures — in a stream H_2 and PH_3 to prevent destruction of the semiconductor. Figure 1, *a* shows the dependence of the photoluminescence intensity of the $GaInP_2$-InP QD layer on the annealing temperature. It can be seen that of all the selected options, SiN_x demonstrates the best temperature stability. Also, the SiO_2, obtained by thermal evaporation, remains stable up to 600°C.

In addition to temperature stability, the most important parameter is the preservation of the $GaInP_2$ epitaxial surface for further overgrowth. Our experiments have shown that contact with many materials reduces the PL QD intensity. Figure 1, *b* shows the spectra of QDs grown on the surface after removing the SiO_2 layer, as well as a control sample on the $GaInP_2$ surface without any treatment (reference). It can be seen that the use of liquid etching practically does not affect the quality of the resulting structures. At the same time, the use of Ar^+ plasma to remove the dielectric leads to the formation of defects on the surface of the layer, which is accompanied by strong quenching of the PL signal. Other combinations of materials and etching methods led to a noticeable decrease in the PL intensity of $GaInP_2$ and or QD. The use of SiN_x results in the absence of a QD signal while maintaining the intensity of $GaInP_2$. Previously, our studies showed that the growth of QD by the SAE method is possible only at a temperature reduced to 600°C, since at a higher temperature the relaxation of elastic stresses does not lead to the formation of QD, but occurs along the edge of the aperture [6]. Thus, the temperature stability of the SiO_2 layer obtained by thermal evaporation turns out to be sufficient.

Figure 2, *a* shows an image of QD grown in an aperture in a SiO_2 film. Figure 2, *b* shows the PL spectra (two random points inside one aperture) at 8 K, demonstrating the signal from the QD. The use of an electron lithograph in conjunction with liquid etching allows to reduce the aperture size to 500 nm (Figure 2, *a*), which does not solve the problem of obtaining a single QD. This is due to the need for significant overexposure of the sample in the etchant, which causes the pattern to be rasterized (from 100 to 500 nm). Lift-off lithography can be used to reduce the size of apertures. We used a sequence with deposition of SiO_2 and SiN_x layers, which is realized due to the difference in the BOE etching rate of thermally deposited SiO_2 and SiN_x deposited by a hot plasma-chemical method. The mask is formed in the SiN_x layer, but the epitaxial surface of the aperture is obtained without contacting it. The SiO_2 layer, as in the previous case, had a thickness of 100 nm. The thickness of the SiN_x layer was chosen in such a way as to ensure the opportunity of opening the apertures and was 10 nm. At the first step, a layer of SiO_2 was deposited, from which cylinders were subsequently formed by electron-beam lithography. To remove the dielectric, the method of

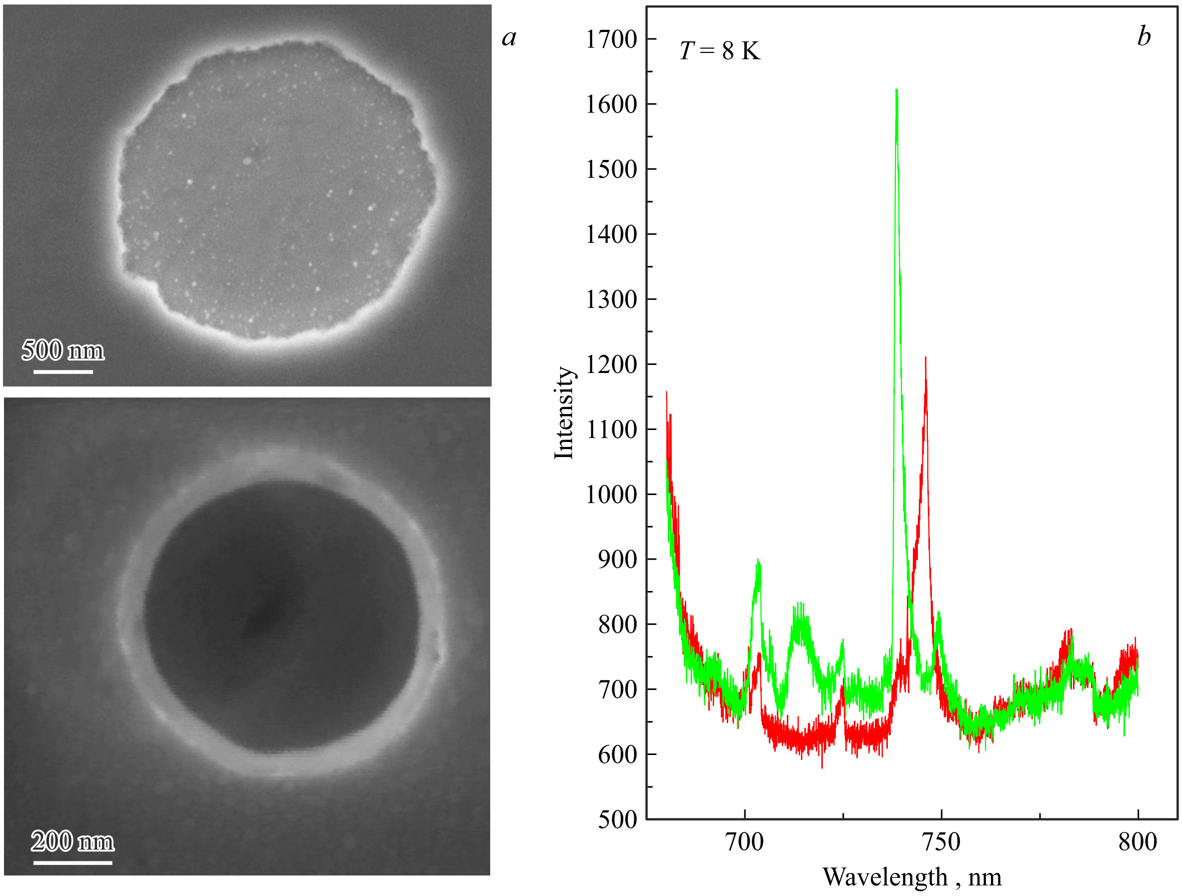

Figure 2. *a* — SEM images of a QD aperture obtained by photolithography and liquid etching (top), and an aperture obtained by electron-beam lithography (100 nm figure) and liquid etching (bottom); *b* — examples of PL spectra of QD inside the aperture. (The colored version of the figure is available on-line).

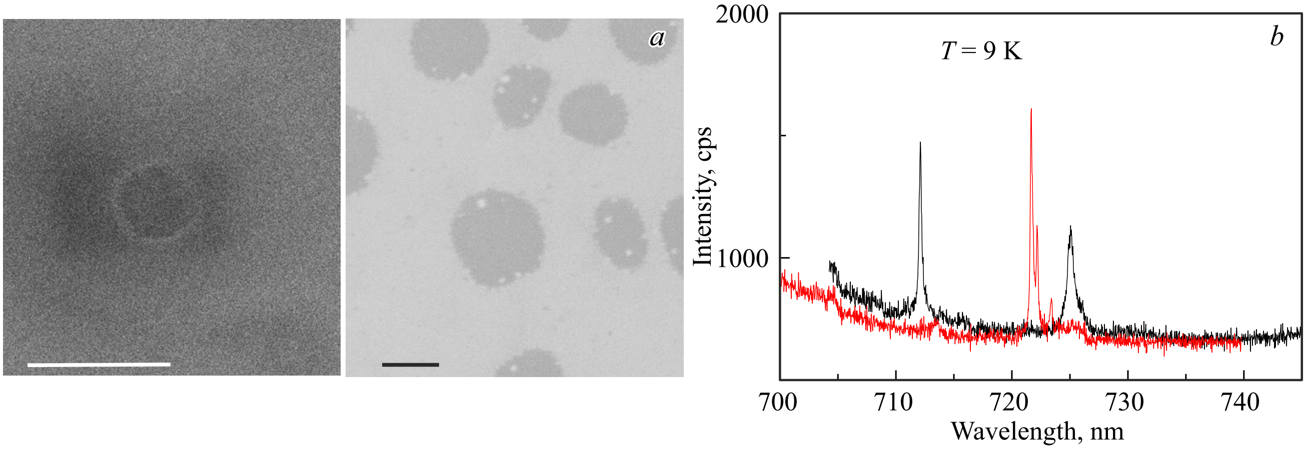

Figure 3. *a* — image of a 90 nm aperture obtained by liquid etching and lift-off lithography (left), and the same sample after growing InP QDs (right) and its PL spectra (*b*). The scale bar in the images corresponds to 200 nm.

plasma-chemical etching CF_4 was used. The next step was to deposit a layer of SiN_x and open the apertures using the liquid etching method BOE.

Figure 3, *a* shows apertures obtained by lift-off lithography. The diameter of the apertures is 90 nm. A QD layer was deposited on this sample. Figure 3, *b* shows the photoluminescence spectrum of such a sample. As can be seen, a stable PL signal is maintained as the procedure becomes more complex; however, in the presented sample, during QD growth, the SiN_x film ruptured with the formation of many apertures for parasitic growth (Figure 3, a). The obtained result demonstrates the opportunity of implementing spatially selective growth in the $GaInP_2$-InP system for obtaining single QD. Optimizing the thickness of the dielectric layers should ensure the stability of the SiN_x film.

4. Conclusion

The conducted studies showed the promise of the developed approach for the spatially selective growth of QD in the $GaInP_2$-InP system using MOVPE epitaxy. It has been shown that preservation of the epitaxial properties of the surface can be achieved through the use of thermally deposited SiO_2, which has the best stoichiometry and temperature stability. For dielectric removal, the preferred method is wet etching with a buffered HF solution. It has been experimentally shown that achieving minimal aperture sizes is possible by using the lift-off lithography method using a SiO_2 layer as an auxiliary layer and a SiN_x layer as a mask material.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] B. Wang, Yu. Zeng, Yu. Song, Y. Wang, L. Liang, L. Qin, J. Zhang, P. Jia, Y. Lei, Ch. Qiu, Y. Ning, L. Wang. Crystals, **12** (7), 1011 (2022).

[2] J. Wong-Leung, I. Yang, Z. Li, S.K. Karuturi, L. Fu, H.H. Tan, Ch. Jagadish. Adv. Mater., **32**, e1904359 (2020).

[3] X. Yuan, D. Pan, Y. Zhou, X. Zhang, K. Peng, B. Zhao, M. Deng, J. He, H.H. Tan, Ch. Jagadish. Appl. Phys. Rev., **8**, 021302 (2021).

[4] L. Guniat, Ph. Caroff, A.F. Morral. Chem. Rev., **119**, 8958 (2019).

[5] A.M. Mintairov, D.V. Lebedev, A.S. Vlasov, A.O. Orlov, G.L. Snider, S.A. Blundell. Sci. Rep., **11**, 21440 (2021).

[6] A.S. Vlasov, A.V. Ankudinov, N.A. Kalyuzhnyy, D.V. Lebedev, S.A. Mintairov, R.A. Salii, I.S. Mukhin, A.M. Mozharov, A.M. Mintairov. AIP Conf. Proc., **2300**, 020130 (2020).

Translated by Ego Translating