MATERIALS PHYSICS AND MECHANICS RESEARCH ARTICLE

Submitted: October 21, 2024 **Revised: November 13, 2024** **Accepted: December 2, 2024**

Spalling-induced β-Ga_2O_3 lift-off protocol

P.N. Butenko ✉, A.V. Chikiryaka, M.E. Boiko, L.I. Guzilova, V.M. Krymov, B.A. Obidov, R.B. Timashov, S.V. Shapenkov, M.D. Sharkov, V.I. Nikolaev

Ioffe Institute, St. Petersburg, Russia

✉ pavel.butenko@mail.ioffe.ru

ABSTRACT

Fabrication of gallium oxide 1–100 μm-thick layers by exfoliation them from single crystals opens up the way to provide good thermal management in high-power Ga_2O_3 devices. Here we propose a lift-off protocol based on spalling of homoepitaxial layers from (100) β-Ga_2O_3 bulk crystal. The process includes sputtering of Ni sacrificial mask on β-Ga_2O_3 substrate and its modification by annealing, prior to epitaxial layer deposition in mist-CVD reactor. The separated 4 μm-thick β-Ga_2O_3 layers have been studied. It is shown that implementation of the lift-off protocol allows obtaining high-quality free-standing layers.

KEYWORDS

gallium oxide • thick layers • single crystals • exfoliation • lift-off • mist-CVD • free-standing layers

Acknowledgements. *P.N. Butenko and L.I. Guzilova gratefully appreciate the Russian Science Foundation for financial support project No. 23-29-10196.*

Citation: Butenko PN, Chikiryaka AV, Boiko ME, Guzilova LI, Krymov VM, Obidov BA, Timashov RB, Shapenkov SV, Sharkov MD, Nikolaev VI. Spalling-induced β-Ga_2O_3 lift-off protocol. *Materials Physics and Mechanics*. 2024;52(5): 55–63.
http://dx.doi.org/10.18149/MPM.5252024_6

Introduction

Growth of the bulk β-Ga_2O_3 crystals is still a complex task, which only a few research groups in the world have successfully accomplished to some extent. This is evidenced by the fact that the only company that has achieved a commercial result to date is Tamura Corp. [1], whose substrates remain extremely expensive. In fact, bulk Ga_2O_3 crystals are grown exclusively from-melt techniques, which in this case have a number of drawbacks. First of all, the temperature distribution in both the crystallization zone and the melt region is unstable due to the multifactorial nature of the process, which is difficult to model. One of these factors is the step-by-step dissociation of gallium oxide into lower oxides and ultimately into O_2 and Ga, which is noticeable already at 1200 °C [2]. In addition, oxygen released during the decomposition of Ga_2O_3 deteriorates the growth zone equipment during chemical interaction, and free gallium forms an intermetallic compound with iridium. For this reason, the extremely expensive iridium used in the Czochralski process [3] (CZ) or Stepanov edge-defined film-fed growth (EFG) [4] techniques become a consumable. To fabricate *epi-ready* substrates, expensive bulk crystals must be subjected to post-growth processing (cutting, grinding, polishing), during which the material is underwent to mechanical and thermal effects. It has been experimentally established [5] that the structure of the subsurface layers of *epi-ready* substrates has a lower degree of crystal perfection than the bulk and contains defects, for

example, in the form of threading dislocations due to post-growth processing. In addition to being highly anisotropic material in its physical properties, gallium oxide suffers from low thermal conductivity that emerges for substrate thicknesses of 500 μm and more [4]. These are the thicknesses of the substrates cut from the grown ones (in the form of boules), which is limited by the cutting capabilities. Obviously, this limits the scope of application of the material in power electronic devices.

Ground on this, an idea of development of bulk free-standing gallium oxide layers looks highly attractive. One of the most effective approaches from the collection of lift-off techniques is the use of a sacrificial interlayer. The main challenge of this layer is to form a weakened interface to accomplish detachment. There are number examples are known among such semiconductor materials as: GaAs [6,7], InP [8], GaN [9–23]. The majority of authors employ epitaxial growth to obtain the upper layer that will be subjected for exfoliation. The novel mist chemical-vapor-deposition is one of the few techniques that allows growth of the thick gallium oxide layers at high growth rates [24–26]. This method is cost-effective and provides flexible doping schemes, precise layer thickness control and high crystal perfection.

In this paper, we report the lift-off procedure by spalling (100) β-Ga_2O_3 homoepitaxial layers grown by mist-CVD for the first time. A modified Ni film was used as a sacrificial interlayer. Fabrication of a such a Ni-droplet mask pursues two goals: to provide further growth process according epitaxial lateral overgrowth (ELOG) technique and to employ it as a sacrifice layer that weakens the following exfoliation spalling.

Materials and Methods

(100) oriented β-Ga_2O_3 plates were used as the host-substrates. Previously the cylindric boule was grown in our lab by Czochralski process (Cz). The setup and the process parameters can be found in our recent publications [27–30]. Since (100) is a gallium oxide perfect cleavage plane, blocks splitting occurs precisely along it. Thus, the boule was cleaved manually into close-to-rectangular plates measuring approximately to 2 × 1 cm^2 and 2 mm thick. The plates that had plane surfaces without chip outs were selected. It is known that (100) β-Ga_2O_3 surface inherent interlaced patchwork morphology with 20–200 mm size regions that are highly smooth [27]. Therefore, such regions are adapted for epitaxial growth.

Vacuum thermal evaporation (VTE) at VUP-2KU4.2 was applied to sputter Ni sacrifice layer prior to homoepitaxy process. The Ni foil (99.8 % purity) divided into 0.0034 g portions per one sputtering process was used. The Ni portion weight was measured with a help of a Radwag WAS 220/C/2 analytical balance to provide Ni layer thickness of ~200 nm. The correspondence between film thickness and film weight was determined experimentally in advance. The evaporation process was performed at partial pressure of 10^{-5} Pa and a voltage of 60 V applied to the W-filament. To form self-ordered droplet-like island arrays, the subsequent thermal annealing was used. The improved Granat vacuum chamber was utilized. The annealing was performed at 1200 °C for 30 min in Ar ambient (at $2 \cdot 10^4$ Pa). The verification of the Ni layer thickness proceeded by registration the difference in the contrast of the grown layer from the base in the scanning electron microscope (SEM) on a scratch. It was mechanically applied to the sputtered

layer using a needle, the depth of which was registered by a microscope relative to the top surface of the layer.

The epitaxial growth was developed on the (100) Ni/β-Ga_2O_3 substrate by the mist-CVD technique. The home-made mist-CVD reactor employed a process based on acetylacetonate (acac). The growth temperature and duration were 950 °C and 3 h, correspondingly. The detailed process parameters can be found in our previous paper [31].

The thicknesses of the homoepitaxial layers were measured by defining a difference in weights (recalculated through the layer volume and β-Ga_2O_3 density) of the Ni/β-Ga_2O_3 wafer and this sample (β-Ga_2O_3/Ni/β-Ga_2O_3) after growth. The Snoll 4/1300 muffle furnace was employed for sample annealing to weaken the Ni interface and impel epitaxial layer exfoliation. The annealing mode was set as 30 min at 700 °C on air. Directly for the exfoliation process the 3M Scotch double-sided tape was utilized. To get read of the rest of the Ni interlayer the sample was etched with HNO_3 for 10 min at 30 °C [32]. The complete scheme of (100) β-Ga_2O_3 the lift-off is shown in Fig. 1.

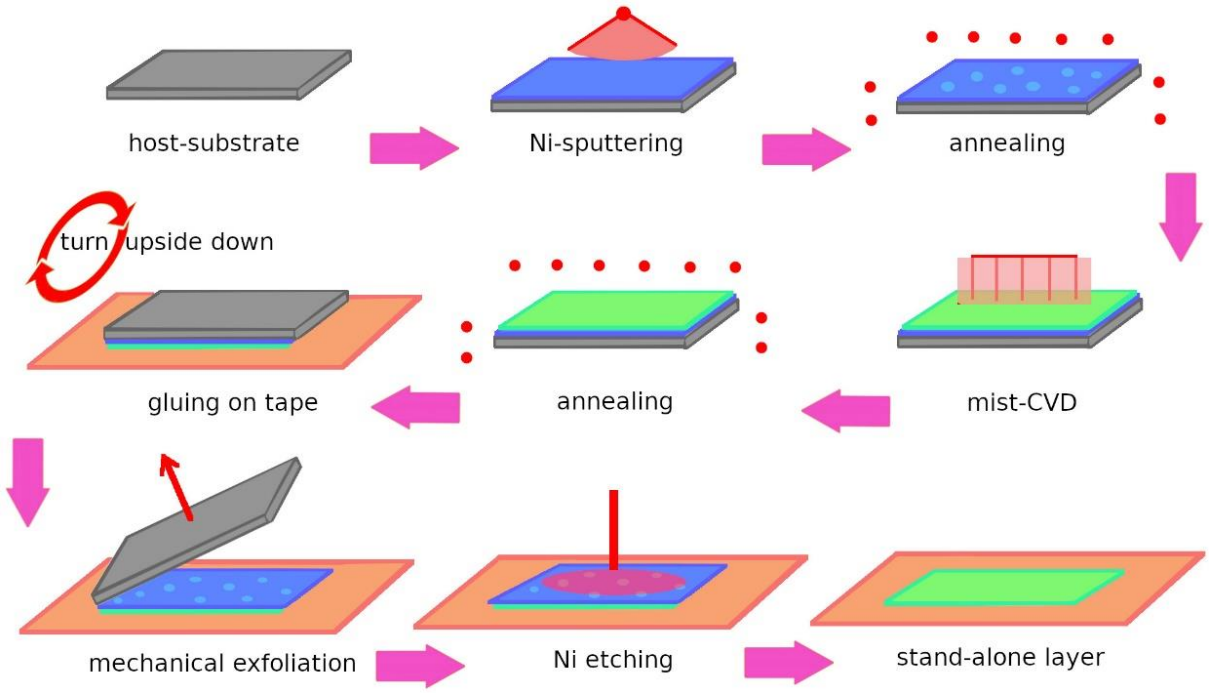

Fig. 1. The complete scheme of (100) β-Ga_2O_3 the lift-off

The surface morphology of the grown gallium oxide layer was analyzed using a Phenom ProX SEM operating in secondary electron (SE) mode at 10 kV. Energy dispersive spectroscopy (EDS) implemented in SEM was applied for chemical characterization. The phase composition and the crystallinity of the homoepitaxial layers were analyzed by X-ray diffraction (XRD) at Bourevestnik DRON-7 setup utilizing equipped with Ge (111) monochromator crystal on doublet Cu $K_{\alpha 1,2}$ radiation, the wavelets 1.5406 Å ($K_{\alpha 1}$) and 1.5444 Å ($K_{\alpha 2}$).

Results and Discussion

The Ni sacrificial layer was sputtered on the (100) surface of the β-Ga_2O_3 substrate. The estimation ground on scratch measurement (see Fig. 2) gave a value of 230 nm which is very close to the experimental evaluation.

At the next step the sample was annealed with an aim to form separate droplets. The surface contains Ni self-organized droplets of 0.5–1 μm in diameter is shown in Fig. 3(a). The chemical composition measured within a droplet region was Ga:Ni:O ≈ 28:29:43 at. %, at the same time in the rest region the Ni concentration appeared to be as below 1 at. % and the chemical formula corresponded to trivalent gallium oxide.

The surface of the sample upon mist-CVD epitaxy is depicted in Fig. 3(b). One can see, that it has relatively homogeneous morphology that consists of facetted crystals of various shapes with sizes of 1–2 μm. The thickness of the grown layer was estimated as 4 μm by weighting based on the β-Ga_2O_3 density ρ = 5.95 g/cm^3 [33].

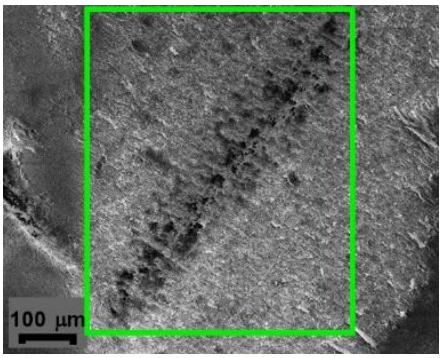

Fig. 2. SEM plan-view image of the Ni layer with a scratch in green square

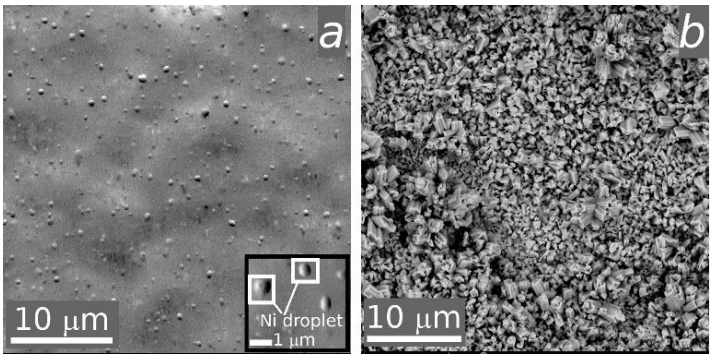

Fig. 3. SEM plan-view images of the (100) β-Ga_2O_3 layer: after Ni sputtering and annealing (a) and after mist-CVD growth (b). The inset the (a) shows the average droplet size of 0.5–1 μm

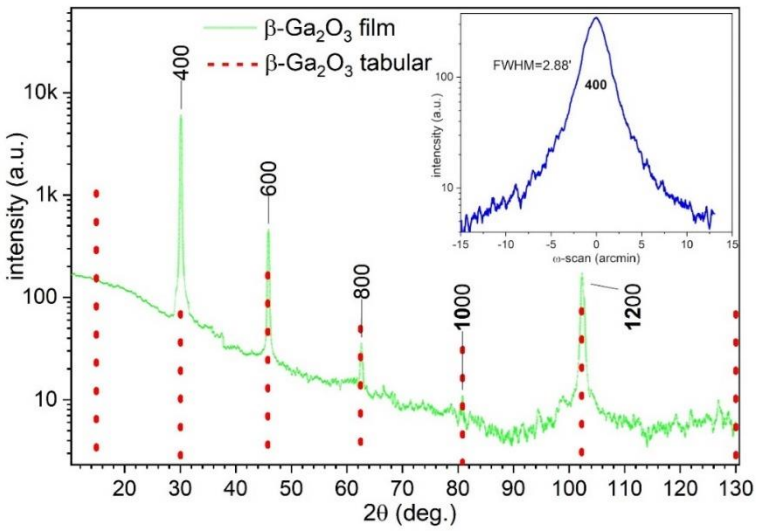

Fig. 4. XRD pattern and ω-scan (the inset) for the (100) β-Ga_2O_3 homoepitaxial layer

The phase composition and the crystal perfection were estimated via θ-2θ curve and the ω-scan, respectively. Figure 4 illustrates a single-crystal structured homoepitaxial [100] oriented β-Ga_2O_3 layer. No additional peaks indicating the presence of other phases

or polycrystalline inclusions were detected. Perfection of the grown layer is confirmed by the successive series of even reflection orders from 400 up to 12 0 0 observed on the X-ray diffraction pattern obtained in the θ-2θ scanning mode (ICDD #00-041-1103). 200 and 14 0 0 reflections are not registered since their intensities are very low themselves as it is shown by pattern modeling [34].

An ω-scan of the 400-peak shown in the inset demonstrated that the rocking curve peak can be effectively fitted via a Gaussian function with the FWHM (full-width-of-half maximum) of less than 3 arcmin. I.e., the crystallinity of the layer can be thus estimated as 2.88 arcmin (see inset of the Fig. 4) which is highly acceptable value for the epitaxial layer. The absence of additional peaks within the incident beam area of 0.1 × 1.0 mm^2 indicates the presence of a coherent β-Ga_2O_3 mosaic of high perfection for this field of study.

Prior to lift-off process, the samples were undergoing annealing for initiating the exfoliating procedure. The exfoliation process was carried out using double-sided tape. The sample was glued to the tape with the epitaxial layer surface (see Fig. 5(a)). The substrate was then pulled upwards to peel off the epitaxial layer (see Fig. 5(b–d)). The most of epitaxial layers were successfully detached using this approach.

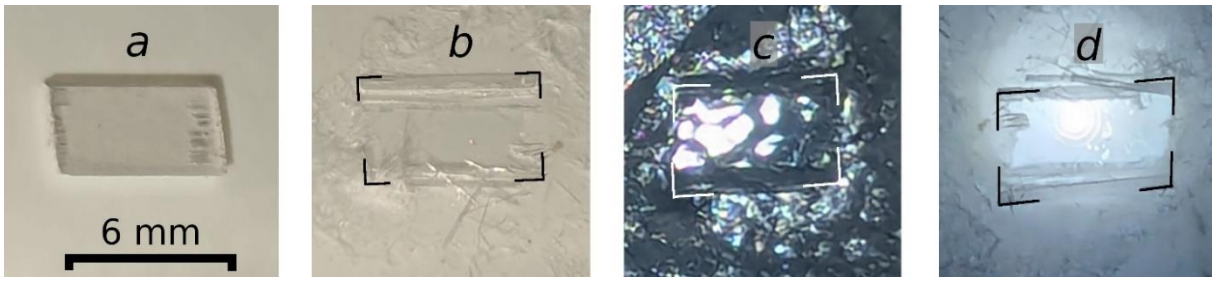

Fig. 5. Exfoliation process: the sample glued to the tape with the epitaxial layer surface (a), the peeled off epitaxial layer (b), the same in reflected light (c), the same in transmitted light (d). The silhouette of the epitaxial layer is indicated by the frame. The scale of all images is the same

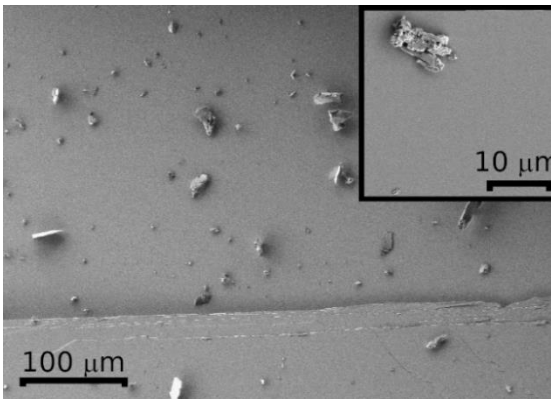

Fig. 6. SEM plan-view images of the (100) β-Ga_2O_3 stand-alone layer with particularities. A zoomed region is depicted in the inset

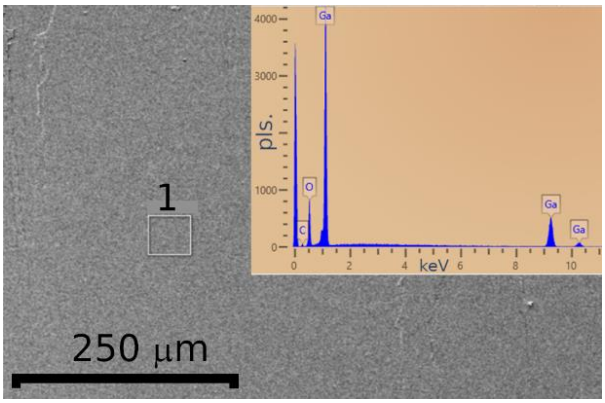

Fig. 7. SEM plan-view images of the (100) β-Ga_2O_3 stand-alone layer upon etching. EDS measurements were registered in the box marked as "1". The inset shows an energy spectrum contains Ga and O peaks only

SEM showed (see Fig. 6) that the contact surface of the exfoliated layer is suffered from uneven morphology, since it may include parts of the sacrificial Ni layer and fragments of gallium oxide itself which is capable of splitting along the cleavage plane. As soon as HNO_3 at room temperature does not affect gallium oxide substrate (unless it is in the form of thin films), but able to dissolve Ni, it was utilized as the etchant.

Upon etching the surface contained no particularities as well as no Ni has been found. This was approved by EDS measurements. The inset in Fig. 7 shows identification of Ga and O only while the white box indicates the scanning area.

The diffraction pattern registered for the spalled layer is depicted in Fig. 8. It shows split (due to the doublet nature of the radiation) reflections 400, 600, 800, 12 0 0, and also 10 0 0, which has the form of a separate peak (probably from the $K_{\alpha1}$ line) with a satellite of reduced intensity (which can be interpreted as a contribution from the $K_{\alpha2}$ component). Processing of the reflections set caused by the $K_{\alpha1}$ radiation component yields the interplanar distance d_{200} (i.e. between adjacent (200) crystallographic planes) of about 11.865 Å. The similar value obtained on treating the reflections formed due to the $K_{\alpha2}$ beam component turned out to be approximately 11.864 Å. The coherent-domain-size (CDS) value happened to be about 170 nm in both cases with a microstrain of no more than 10^{-4}. The set of the peaks in the range of ~ 13–28 deg. obviously belongs to tape material. Profile analysis of the ω-scan curve from the homoepitaxial β-Ga_2O_3 film of thickness 4 μm separated from a single-crystal substrate showed that its perfection (3.77 arcmin for the ω-scan curve FWHM) is close to the one of the unseparated layer (2.88 arcmin, see Fig. 4, the inset). Somewhat broadening and formation of symmetrical steps on both slopes of the ω-scan peak can be associated with its mechanical destruction in separating from the substrate.

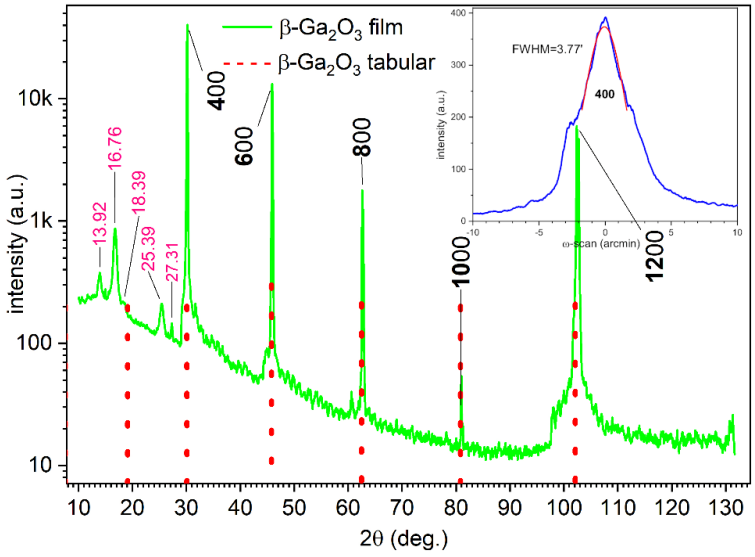

Fig. 8. XRD pattern and ω-scan (the inset) for the (100) β-Ga_2O_3 homoepitaxial layer after spalling

Conclusion

The fabrication of free-standing homoepitaxial (100) β-Ga_2O_3 layer by spalling from the native host-substrate is developed. It includes: 200-nm-thick sacrificial Ni film sputtering by vacuum thermal evaporation; formation of nickel micron scale drop-like mask by high temperature annealing and homoepitaxial growth of 4-μm-thick layer by mist-CVD. The mechanical exfoliation itself was carried out with preliminary annealing. The exfoliated layer is characterized as a coherent β-Ga_2O_3 mosaic structure with high perfection. The measured value of the coherent-domain-size is about 170 nm with a microstrain of no more than 10^{-4}. The full-width-of-a-half-maxima value is amounted as 3.77 arcmin, which is broadened compared to as-grown non-spalled layer (FWHM = 2.88 arcmin) presumably due to mechanically induced destruction. The exfoliated layers have smooth surface, and relatively high crystal quality. We propose that such approach is cost-effective for production of high power devices based on gallium oxide single crystals.

References

1. *World's first successful epitaxial deposition of gallium oxide on a 6-inch wafer using the HVPE method*. Available from: https://www.novelcrystal.co.jp/eng/2022/1107/ [Accessed 10th October 2024].
2. Ueda N, Hosono H, Waseda R, Kawazoe H. Synthesis and control of conductivity of ultraviolet transmitting β-Ga_2O_3 single crystals. *Appl. Phys. Lett.* 1997;70: 3561–3563.
3. Ritter JR, Lynn KG, McCluskey MD. Iridium-related complexes in Czochralski-grown β-Ga_2O_3. *J. Appl. Phys.* 2019;126: 225705.
4. Heinselman KN, Haven D, Zakutayev A, Reese SB. Projected Cost of Gallium Oxide Wafers from Edge-Defined Film-Fed Crystal Growth. *Crystal Growth & Design.* 2022;22(8): 4854–4863.
5. Butenko PN, Guzilova LI, Chikiryaka AV, Boiko ME, Sharkov MD, Almaev AV, Nikolaev VI. Impact on the subsurface layers of the single-crystal β-Ga2O3 wafers induced by a mechanical wear. *Materials Science in Semiconductor Processing***.** 2022;143: 106520.
6. McClelland RW, Bozler CO, Fan JCC. A technique for producing epitaxial films on reuseable substrates. *Appl. Phys. Lett.* 1980;37(6): 560-562.
7. Cheng CW, Shiu KT, Li N, Han SJ, Shi L, Sadana DK. Epitaxial lift-off process for gallium arsenide substrate reuse and flexible electronics. *Nature Communications.* 2012;4: 1577.
8. Park H, Won H, Lim C, Zhang Y, Han WS, Bae SB, Lee CJ, Noh Y, Lee J, Lee J, Jung S, Choi M, Lee S, Park H. Layer-resolved release of epitaxial layers in III-V heterostructure via a buffer-free mechanical separation technique. *Sci. Adv.* 2022;8(3): eabl6406.
9. Hu H, Zhang B, Liu L, Xu D, Shao Y, Wu Y, Hao X. Growth of Freestanding Gallium Nitride (GaN) Through Polyporous Interlayer Formed Directly During Successive Hydride Vapor Phase Epitaxy (HVPE) Process. *Crystals.* 2020;10: 141.
10. Badokas K, Kadys A, Augulis D, Mickevicius J, Ignatjev I, Skapas M, Šebeka B, Juška G, Malinauskas T. MOVPE Growth of GaN via Graphene Layers on GaN/Sapphire Templates. *Nanomaterials.* 2022;12: 785.
11. Fujii K, Lee S, Ha JS, Lee HJ, Lee HJ, Lee SH. Leakage current improvement of nitride-based light emitting diodes using CrN buffer layer and its vertical type application by chemical lift-off process. *Appl. Phys. Lett.* 2009;94(24): 722–747.
12. Horng RH, Pan CT, Tsai TY, Wuu DS. Transferring Thin Film GaN LED Epi-Structure to the Cu Substrate by Chemical Lift-Off Technology. *Electrochem. Solid-State Lett.* 2011;14(7): H281.
13. Víllora EG, Shimamura K, Kitamura K, Aoki K, Ujiie T. Epitaxial relationship between wurtzite GaN and β-Ga_2O_3. *Appl. Phys. Lett.* 2007;90(23): 234102.
14. Wei T, Yang J, Wei Y, Huo Z, Ji X, Zhang Y, Wang J, Li J, Fan S. Cross-stacked carbon nanotubes assisted self-separation of free-standing GaN substrates by hydride vapor phase epitaxy. *Sci. Rep.* 2016;6: 28620.
15. Rogers DJ, Hosseini Teherani F, Ougazzaden A, Gautier S, Divay L, Lusson A. Use of ZnO thin films as sacrificial templates for metal organic vapor phase epitaxy and chemical lift-off of GaN. *Appl. Phys. Lett.* 2007;91(7): 71120.

16. Liu HF, Liu W, Chua SJ. Epitaxial growth and chemical lift-off of GaInN/GaN heterostructures on c- and r-sapphire substrates employing ZnO sacrificial templates. *J. Vac. Sci. Technol. A.* 2010;28(4): 590–594.
17. Tsai TY, Horng RH, Wuu DS, Ou SL, Hung MT, Hsueh HH. GaN Epilayer Grown on Ga_2O_3 Sacrificial Layer for Chemical Lift-Off Application. *Electrochem. Solid. ST.* 2011;14(11): H434–H437.
18. Tsai TY, Ou SL, Hung MT, Wuu DS, Horng RH. MOCVD growth of GaN on sapphire using a Ga_2O_3 interlayer. *J. Electrochem. Soc.* 2011;158(11): H1172–H1178.
19. Park J, Song KM, Jeon SR, Baek JH, Ryu SW. Doping selective lateral electrochemical etching of GaN for chemical lift-off. *Appl. Phys. Lett.* 2009;94: 221907.
20. Lin CF, Dai JJ, Wang GM, Lin MS. Chemical lift-off process for blue light-emitting diodes. *Appl. Phys. Express.* 2010;3(9): 2101.
21. Lin CF, Dai JJ, Lin MS, Chen KT, Huang WC, Lin CM, Jiang RH, Huang YC. An AlN sacrificial buffer layer inserted into the GaN/patterned sapphire substrate for a chemical lift-off process. *Appl. Phys. Express.* 2014;3(3): 031001.
22. Horng RH, Hsueh HH, Ou SL, Tsai CT, Tsai TY, Wuu DS. Chemical lift-off process for nitride LEDs from an Eco-GaN template using an AlN/strip-patterned-SiO_2 sacrificial layer. *Phys. Stat. Sol.* 2017;214(3): 1600657.
23. Hsueh HH, Ou SL, Wuu DS, Horng RH. InGaN LED fabricated on Eco-GaN template with a Ga_2O_3 sacrificial layer for chemical lift-off application. *Vacuum.* 2015;118: 8–12.
24. Zuo Y, Feng Q, Zhang T, Tian X, Li W, Li J, Zhang C, Zhang J, Hao Y. A Novel Method for Growing α-Ga2O3 Films Using Mist-CVD Face-to-face Heating Plates. *Nanomaterials.* 2023;13(1): 72.
25. Zhang Z, Yan P, Song Q, Chen H, Zhang W, Yuan H, Du F, Liu D, Chen D, Zhang Y. Recent progress of Ga2O3 materials and devices based on the low-cost, vacuum-free Mist-CVD epitaxial growth method. *Fundamental Research.* 2024;4(5): 1292-1305.
26. Vasin AV, Yatskiv R, Černohorský O, Bašinová N, Grym J, Korchovyi A, Nazarov AN, Maixner J. Challenges and solutions in Mist-CVD of Ga2O3 heteroepitaxial films. *Materials Science in Semiconductor Processing.* 2025;186; 109063.
27. Butenko PN, Boiko ME, Guzilova LI, Krymov VM, Shapenkov SV Sharkov MD, Verbitskii VN, Zarichny AA, Nikolaev VI. Enhancing the perfection of bulk (100) β-Ga2O3 crystals grown by Czochralski method. *J. Cryst. Growth.* 2024;630: 127597.
28. Butenko PN, Boiko ME, Sharkov MD, Almaev AV, Kitsay AA, Krymov VM, Zarichny AA, Nikolaev VI. High-temperature annealing of (201) β-Ga2O3 substrates for reducing structural defects after diamond sawing, *J. Semiconductors.* 2023;44: 122801,
29. Zarichny AA, Butenko PN, Boiko ME, Sharkov MD, Nikolaev VI. The analysis of the etch pits parameters in the (201) plane of the β-Ga2O3 substrate crystals. *Materials Physics Mechanics.* 2023;51(3): 46–51.
30. Butenko PN, Timashov RB, Boiko ME, Guzilova LI, Shapenkov SV, Sharkov MD, Sergienko ES, Stepanov AI, Nikolaev VI. Thick β-Ga2O3 homoepitaxial films grown on (201) substrate by mist-CVD. *Materials Today Communications.* 2024;41: 110970.
31. Butenko PN, Timashov RB, Stepanov AI, Pechnikov AI, Chikiryaka AV, Guzilova LI, Stepanov SI, Nikolaev VI. *Condensed Matter and Interphases.* 2023;25(4): 542.
32. *Metallographic Products for Sample Preparation and Analysis.* Available from: https://www.metallographic.com/ [Accessed 10th October 2024].
33. Stepanov SI, Nikolaev VI, Bougrov VE, Romanov AE. Gallium oxide: Properties and applications: a review. *Rev. Adv. Mater. Sci.* 2016;44(1): 63–86.
34. Persson K. *Materials Data on Ga_2O_3 (SG:12) by Materials Project.* Available from: https://doi.org/10.17188/1312771 [Accessed 10th October 2024].

About Authors

Pavel N. Butenko
Candidate of Technical Sciences
Senior Researcher (Ioffe Institute, St Petersburg, Russia)

Andrew V. Chikiryaka
Researcher (Ioffe Institute, St Petersburg, Russia)

Michael E. Boiko
Candidate of Physical and Mathematical Sciences
Senior Researcher (Ioffe Institute, St Petersburg, Russia)

Liubov I. Guzilova
Candidate of Physical and Mathematical Sciences
Researcher (Ioffe Institute, St Petersburg, Russia)

Vladimir M. Krymov
Candidate of Physical and Mathematical Sciences
Senior Researcher (Ioffe Institute, St Petersburg, Russia)

Barzu A. Obidov
Candidate of Physical and Mathematical Sciences
Researcher (Ioffe Institute, St Petersburg, Russia)

Roman B. Timashov
Researcher (Ioffe Institute, St Petersburg, Russia)

Sevastian V. Shapenkov
Candidate of Physical and Mathematical Sciences
Researcher (Ioffe Institute, St Petersburg, Russia)

Michael D. Sharkov
Candidate of Physical and Mathematical Sciences
Senior Researcher (Ioffe Institute, St Petersburg, Russia)

Vladimir I. Nikolaev
Candidate of Physical and Mathematical Sciences
Head of laboratory, Leading Researcher (Ioffe Institute, St Petersburg, Russia)