05

Czochralski growth of semi-insulating bulk iron-doped β-Ga_2O_3 crystals with a resistivity of 160 $G\Omega \cdot cm$

© D.A. Bauman[1], D.Yu. Panov[1], V.A. Spiridonov[1], P.A. Bogdanov[1], A.Yu. Ivanov[1], V.V. Lundin[2], E.Yu. Lundina[3], A.F. Tsatsulnikov[2,4], A.E. Romanov[1,2], P.N. Brunkov[2]

[1] ITMO University, St. Petersburg, Russia
[2] Ioffe Institute, St. Petersburg, Russia
[3] OOO „Monolum", Saint-Petersburg, Russia
[4] Submicron Heterostructures for Microelectronics, Research & Engineering Center, RAS, Saint-Petersburg, Russia
E-mail: dabauman@itmo.ru

Received October 2, 2024
Revised November 5, 2024
Accepted November 8, 2024

In this work, bulk crystals of gallium oxide β-Ga_2O_3 doped with iron were grown by the Czochralski method. Analysis of X-ray diffraction spectra confirmed the presence of only the β--phase and high crystalline quality. The measured specific resistance was 160 $G\Omega \cdot cm$.

Keywords: Bulk crystals, gallium oxide, semi-insulating substrates.

DOI: 10.61011/TPL.2025.03.60720.20137

Wide-band semiconductors are now actively used in such high-tech and economically critical fields as electric power engineering, mechanical engineering, space technology, and sensorics. In fact, they are the basis of modern power electronics and optoelectronics. Over the last decade, the creation of semiconductor devices based on gallium oxide, primarily its most stable β-phase (β-Ga_2O_3) has become of particular interest. This material has a number of advantages over existing wide-band semiconductors: a large bandgap width (4.8 eV [1]), high electric breakdown field ($8\,MV \cdot cm^{-1}$ according to theoretical estimates [2] and more than $4\,MV \cdot cm^{-1}$ according to experimentally obtained data [1]), sufficiently high electron mobility (more than $190\,cm^2/(V \cdot s)$ [3]), transparency in the-range. The field of its promising applications is quite wide: first of all, these are high-voltage metal-oxide-semiconductor (MOS)-transistors, solar-blind UV photodetectors-Schottky diodes, gas sensors [4].

One of the important advantages of β-phase gallium oxide is the possibility of obtaining relatively cheap proprietary substrates from bulk crystals grown from the melt by the methods of Czochralski [5], Stepanov [6] or Bridgman [7].

The combination of the possibility of fabricating proprietary substrates, on the one hand, and characterization values that provide the possibility of creating high-voltage field-effect transistors, on the other hand, leads to the necessity of fabricating semi-insulating gallium oxide substrates with high values of resistivity. It is well known that in the manufacture of MOS transistors with lateral geometry, the key element is a high-resistance layer under the channel, which provides a sharp current cutoff in the devices. This problem is solved by using a semi-insulating substrate for traditional wide-gap semiconductors — silicon carbide [8] and gallium nitride [9]. There are examples of using semi-insulating gallium oxide substrates in the fabrication of field-effect transistors based on β-Ga_2O_3 [10,11]. Therefore, it is an important task to work out the fabrication technology of semi-insulating gallium oxide with controlled values of resistivity.

In this study, samples of bulk crystals β-Ga_2O_3doped with iron were obtained by the Czochralski method. The samples showed high crystalline material quality and significant values of resistivity.

Bulk crystals were grown in the „Nika-3" unit (EZAN, Russia) designed for crystal growth by the Czochralski and Stepanov methods. The initial blend to be melted was gallium oxide powder of 99.999 % purity. For alloying, iron oxide powder (Fe_2O_3) with a purity of 99.99 % was added to the blend. The mass fraction of iron in the blend was 0.011 %. The growth was carried out at a temperature of about 1850 °C and a pressure of 1.4 bar in a mixture of gases ($Ar+O_2$), the oxygen content in the growth atmosphere was about 5 vol.%. The pulling rate of the crystal from the melt was 0.15 mm/min. For analysis and measurements, a 0.5 mm thick wafer with linear dimensions of 10×10 mm was poked along the lattice plane (100) from the central part of the grown bulk crystal (ingots). The poking method is described in detail in [12]. The crystalline quality of the obtained material was investigated by X-ray diffractometry on a DRON-8 unit (NPO „Burevestnik", Russia) in a narrow-gap configuration with a sharp-focus tube with a copper anode and a NaI (Tl) scintillation detector and a Ni-filter. Tansmission spectra were obtained on an AvaSpec-2048 spectrophotometer. Volt-ampere characteristics (VACs) were obtained using a Keithley 6487 voltammeter (lower current limit — 10^{-12} A). The Ti/Au ohmic contacts were formed by thermal sputtering in vacuum. The pressure in

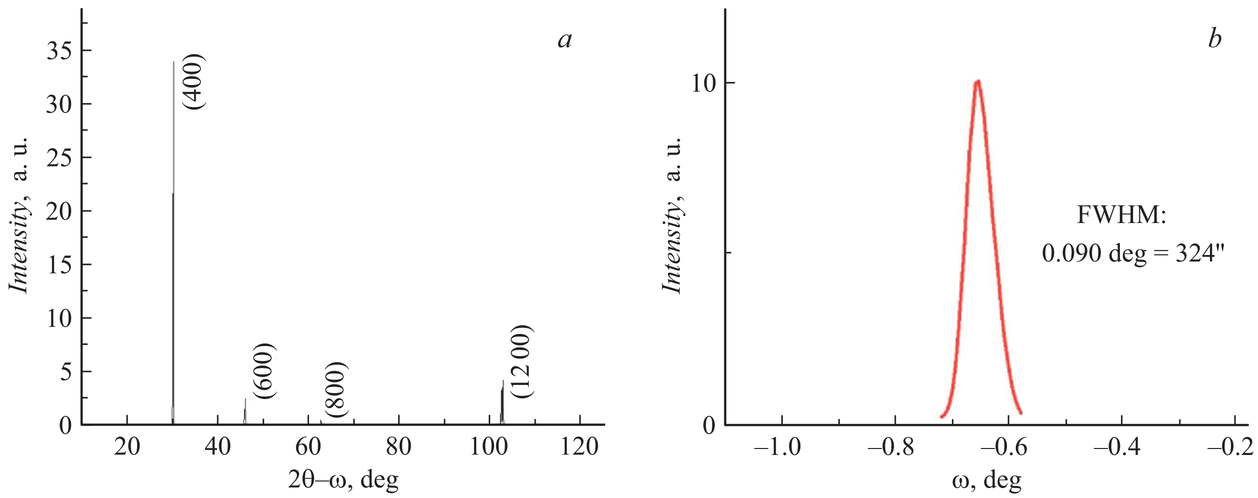

Figure 1. X-ray diffraction spectra of sample β-Ga_2O_3:Fe. *a* — $2\theta{-}\omega$-curve corresponding to the β-phase of gallium oxide, *b* — the swing curve for the reflection from the (400) plane.

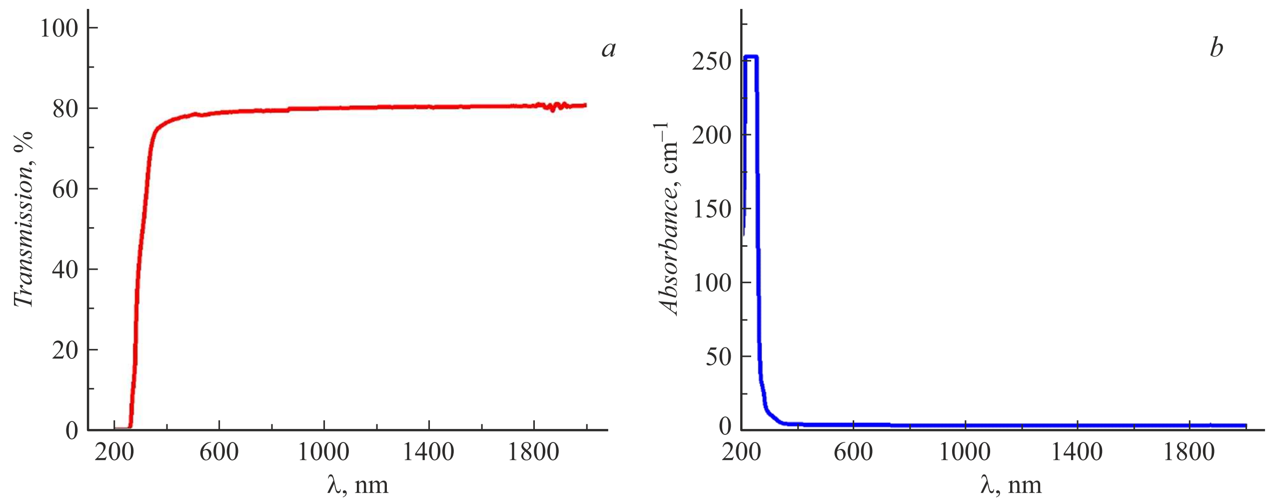

Figure 2. The optical characteristics of the sampleβ-Ga_2O_3:Fe. *a* — optical transmission spectrum, *b* — absorption coefficient.

the chamber at the time the sputtering was started was $8.7 \cdot 10^{-10}$ bar. After sputtering of the contact layers, they were ignited in nitrogen atmosphere at the temperature of $600\,^\circ$C.

The X-ray diffraction curves obtained on the wafer poked out for analysis are shown in Fig. 1. Curve $2\theta{-}\omega$ confirms the presence of only β-phase of gallium oxide in the crystal. The half-width of the X-ray swing curve at reflection from the (400) plane was 0.059 deg, which indicates a sufficiently high crystalline quality.

It is known that bulk crystals β-Ga_2O_3, grown from the melt without special doping possess background doping of *n*-type due to the incorporation of silicon from the initial blend into the crystal. Our evaluations showed that the background *n* electron concentration in the grown crystal is $5 \cdot 10^{17}{-}10^{18}\,cm^{-3}$. The measurements were performed using the Hall effect with the van der Pauw four-probe method on a sample of five unalloyed (unintentionally doped) samples β-Ga_2O_3, in the form of thin 0.3–0.4 mm) thick) wafers averaged over the sample area. Therefore, the manufacture of the semi-insulating material is reduced to the necessity of donor compensation and binding of free electrons by a properly selected p-type impurity. Based on this, the amount of iron in the melt was selected: to minimize the amount of impurity as much as possible, which at the same time is guaranteed to compensate the n-type impurity and the available electrons.

Fig. 2, *a* shows the optical transmission spectra of β-Ga_2O_3:Fe, Fig. 2, *b* — the absorption coefficient. It is easy to notice that there is no decrease in the transmission coefficient in the long wavelength region, which is characteristic of the undoped (unintentionally doped) β-Ga_2O_3 [5,13] and is related to absorption at free electrons. This qualitatively confirms the binding of free electrons by the p-type impurity Fe in the obtained crystal.

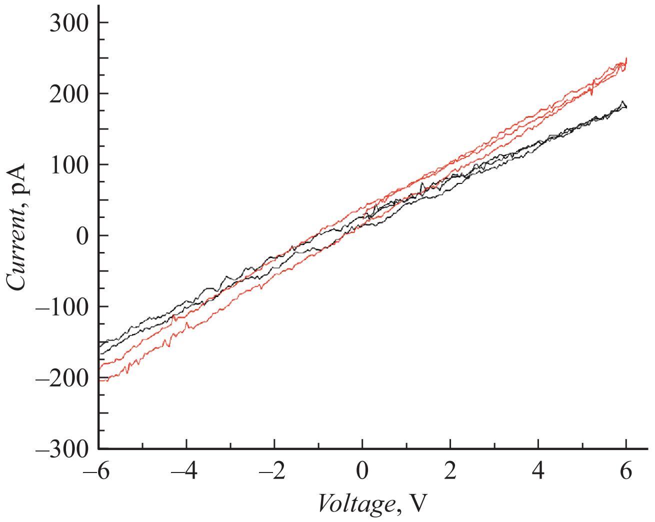

Figure 3. Volt-ampere characteristics obtained on a thin sample. The current direction was along the crystallographic direction [100].

A VAC was obtained to evaluate the specific electrical resistivity. In first experiments to obtain the VAC, the contacts were applied side by side on one side of the sample, and the distance between them was on the order of hundreds of micrometers. However, the resistivity of the sample was so great that it was difficult to obtain reliable results with this contact geometry because the current values were in the region of the sensitivity limit of the instruments. Reducing the distance between the contacts to units of micrometers would inevitably require the application of protective coatings guaranteed to suppress leakage on the surface, so we switched to measurements with current flow across the thin sample. To do this, a thin ($30\,\mu$m) layer was mechanically separated from the sample, a solid contact was sputtered on one side of the sample, and then circular contact pads with a diameter of about 1.2 mm were sputtered on the other side of the sample through a shadow mask. The current path between the contacts through the volume of the material was tens of micrometers, and across the surface amounted to a few millimeters. Therefore, the surface current was negligibly small compared to the measured transverse current. The resulting voltage dependence of the current is shown in Fig. 3.

Calculation taking into account the contact geometry and the VAC data gives a resistivity value of $160\,\mathrm{G\Omega \cdot cm}$. This exceeds the typical resistivity values of commercially produced semi-insulating substrates β-Ga_2O_3 [14] and is sufficient for manufacturing high-voltage MOS-transistors.

Funding

This study was supported by the Russian Science Foundation (project No. 24-12-00229).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J.A. Spencer, A.L. Mock, A.G. Jacobs, M. Schubert, Y. Zhang, M.J. Tadjer, Appl. Phys. Rev., **9**, 011315 (2022). DOI: 10.1063/5.0078037

[2] Shivani, D. Kaur, A. Ghosh, M. Kumar, Mater. Today Commun., **33**, 104244 (2022). DOI: 10.1016/j.mtcomm.2022.104244

[3] A. Bhattacharyya, C. Peterson, T. Itoh, S. Roy, J. Cooke, S. Rebollo, P. Ranga, B. Sensale-Rodriguez, S. Krishnamoorthy, APL Mater., **11** (2), 021110 (2023). DOI: 10.1063/5.0137666

[4] A.A. Petrenko, Ya.N. Kovach, D.A. Bauman, M.A. Odnoblyudov, V.E. Bougrov, A.E. Romanov. Rev. Adv. Mater. Tech., **3** (2), 1 (2021). DOI: 10.17586/2687-0568-2021-3-2-1-26

[5] D.A. Zakgeim, D.I. Panov, V.A. Spiridonov, A.V. Kremleva, A.M. Smirnov, D.A. Bauman, A.E. Romanov, M.A. Odnoblyudov, V.E. Bougrov, Tech. Phys. Lett., **46**, 1144 (2020). DOI: 10.1134/S1063785020110292.

[6] D.A. Bauman, D.I. Panov, V.A. Spiridonov, A.V. Kremleva, A.E. Romanov, Func. Mater. Lett., **16** (7), 2340026 (2023). DOI: 10.1142/S179360472340026X

[7] E. Ohba, T. Kobayashi, T. Taishi, K. Hoshikawa, J. Cryst. Growth, **556**, 125990 (2021). DOI: 10.1016/j.jcrysgro.2020.125990

[8] C.-W. Su, T.-W. Wang, M.-C. Wu, C.-J. Ko, J.-B. Huang, Solid-State Electron., **179**, 107980 (2021). DOI: 10.1016/j.sse.2021.107980

[9] D. Tanaka, K. Iso, R. Makisako, Y. Ando, J. Suda, IEEE Trans. Electron Dev., **71** (5), 3096 (2024). DOI: 10.1109/TED.2024.3375837

[10] A. Bhattacharyya, S. Sharma, F. Alema, P. Ranga, S. Roy, C. Peterson, G. Seryogin, A. Osinsky, U. Singisetti, S. Krishnamoorthy, Appl. Phys. Express, **15**, 061001 (2022). DOI: 10.48550/arXiv.2201.10028

[11] M.J. Tadjer, F. Alema, A. Osinsky, M.A. Mastro, N. Nepal, J.M. Woodward, R.L. Myers-Ward, E.R. Glaser, J.A. Freitas, Jr., A.G. Jacobs, J.C. Gallagher, A.L. Mock, D.J. Pennachio, J. Hajzus, M. Ebrish, T.J. Anderson, K.D. Hobart, J.K. Hite, C.R. Eddy, Jr., J. Phys. D, **54**, 034005 (2021). DOI: 10.1088/1361-6463/abbc96

[12] D.A. Bauman, D.Iu. Panov, D.A. Zakgeim, V.A. Spiridonov, A.V. Kremleva, A.A. Petrenko, P.N. Brunkov, N.D. Prasolov, A.V. Nashchekin, A.M. Smirnov, M.A. Odnoblyudov, V.E. Bougrov, A.E. Romanov, Phys. Status Solidi A, **218**, 2100335 (2021). DOI: 10.1002/pssa.202100335

[13] Z. Galazka, J. Appl. Phys., **131**, 031103 (2022). DOI: 10.1063/5.0076962

[14] https://www.novelcrystal.co.jp/eng/wp-content/uploads/2024/08/5025c6a8c3a3723c996927ee1e3e7fa9.pdf

Translated by J.Savelyeva