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The effect of high-temperature annealing on the properties of bulk β-Ga_2O_3 obtained in different growth atmospheres

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ABSTRACT

The work presents the results of the experiments on annealing in air of bulk crystals of gallium oxide grown in Ar+O_2 and CO_2 atmospheres at a temperature of 1400 °C. The annealing time was 5 hours; the time to reach the temperature was 3.5 hours; the cooling time was 20 hours. Annealed samples show increasing of transmission in infrared area of electromagnetic spectrum and decreasing of width of X-ray rocking curve which means the reduction of the number of defects in crystals. Full width at half maximum of rocking curve for annealed samples was almost the same for both atmospheres: $FWHM_a$ = 84 arcsec for sample grown in Ar+O_2 atmosphere and $FWHM_a$ = 80 arcsec for sample grown in CO_2, which means that after annealing, the quality of the samples became comparable, despite the initial difference.

KEYWORDS

β-Ga_2O_3 • bulk crystal • annealing • optical spectroscopy • XRD

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Introduction

Recently, the theme of ultra-wide bandgap (UWBG) semiconductors has been gaining big attention [1–4]. The term UWBG is commonly used to denote semiconductors with a larger band gap E_g than traditional wide bandgap semiconductors such as silicon carbide (E_g=3.2eV [5]) and gallium nitride (E_g=3.4 eV [6]). Usually, compounds III-V (BN, AlN, AlGaN), diamond and compounds based on gallium oxide are considered as UWBG. The bulk crystal of gallium oxide (β-Ga_2O_3) is a semiconductor with a band gap of about 4.8 eV [7,8], with excellent electrical characteristics, such as large breakdown electric field of about 8 MV/cm theoretically [9] and about 3.8 MV/cm in the device [10], high radiation resistance [11] and relatively high electron mobility (up to 200 $cm^2V^{-1}s^{-1}$ [12]). One of the main advantages of gallium oxide over other UWBG semiconductors is the possibility of fabricating bulk crystals by liquid phase growth methods such as the Czochralski method [13–19] and the edge-defined film-fed growth (EFG) method [20–25] used in the industry.

Experiments on the annealing of bulk β-Ga_2O_3 crystals have shown that annealing in an oxygen-containing atmosphere leads to an increase in optical transmission in the IR region and a drop in the concentration of charge carriers [26–28]. During annealing without oxygen, for example in nitrogen [28] or in vacuum [29], the reverse processes occur – the concentration of carriers increases, transmission decreases.

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Previous experiments have shown that increasing the oxygen concentration in the growth atmosphere improves the quality of crystals [30,31], as well as high-temperature annealing in an oxygen-containing atmosphere [26–28,31–33]. In addition, experiments have shown that the properties of the crystal after annealing change significantly at an annealing temperature of 1200 °C and above [31,33]. In this paper, the effect of annealing on gallium oxide crystals grown in different growth atmospheres is evaluated.

Experimental setup and methodology

For this study bulk single crystals of gallium oxide were grown in the industrial facility "Nika-3" (production of EZAN, Russia) using the Czochralski method as described in our previous work [30]. An iridium crucible was used to form the melt. β-Ga_2O_3 crystals were used as seeds. Ga_2O_3 powder with a purity of 99.999 % (5N) was used as a starting material for the formation of the melt. The growths were conducted in an argon atmosphere with the addition of 5 vol. % of oxygen and in CO_2 atmosphere at a pressure of 1.4 bar.

For the studies plane-parallel plates with thicknesses of 1 mm were cut from crystal boule along the cleavage plane (100).

Annealing was conducted in a shaft furnace at a temperature of 1400 °C for 5 hours (the time to reach the temperature was 3.5 hours, the cooling time was 20 hours) in air. Sample for annealing was placed on sapphire substrate in corundum crucible.

Results and Discussion

The main difficulties in obtaining gallium oxide from the melt are the high melting point (1795–1820 °C [16,34]) and melt decomposition into volatile forms during growth in an atmosphere with oxygen deficiency [16]. The decomposition of the gallium oxide melt can be described by the following reactions:

$$2Ga_2O_3 \rightarrow 4GaO\uparrow + O_2\uparrow \quad (1)$$

$$4GaO \rightarrow 2Ga_2O\uparrow + O_2\uparrow \quad (2)$$

$$2Ga_2O \rightarrow 4Ga\uparrow + O_2\uparrow \quad (3)$$

With crystal growth, decomposition leads to a lack of oxygen in the melt, which in turn leads to a violation of stoichiometry in the grown crystal and the formation of oxygen vacancies in crystal. Vacancies in β-Ga_2O_3 lead, for example, to an increase in optical absorption in the IR region of the spectrum [35].

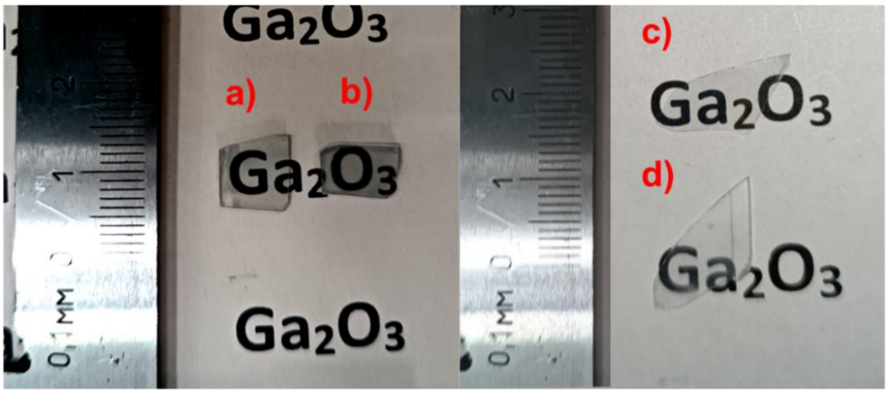

Fig. 1. Photo of the samples of β-Ga_2O_3: a) sample grown in CO_2 atmosphere; b) annealed sample grown in CO_2 atmosphere; c) sample grown in Ar+O_2 atmosphere; d) annealed sample grown in Ar+O_2 atmosphere

After annealing, the sample became visually cloudy (Fig. 1), which indicates a change in the morphology of its top surface, presumably due to diffusion processes. For further experiments, a rough surface layer 0.1 mm thick was exfoliated from each annealed sample and the measurements were carried out on the remaining part of the samples.

Figure 2 shows the normalized transmission spectra of samples. The graph shows that annealing led to an increase in transmission in the IR region of the spectrum, which means a decrease in the number of absorbing centers that can be oxygen vacancies [35]. There is also a strong difference between samples grown in Ar+O_2 and in CO_2 atmosphere, due to the almost five times higher [31] oxygen concentration in the growth atmosphere, which reduces the volatilization of oxygen from the melt [16].

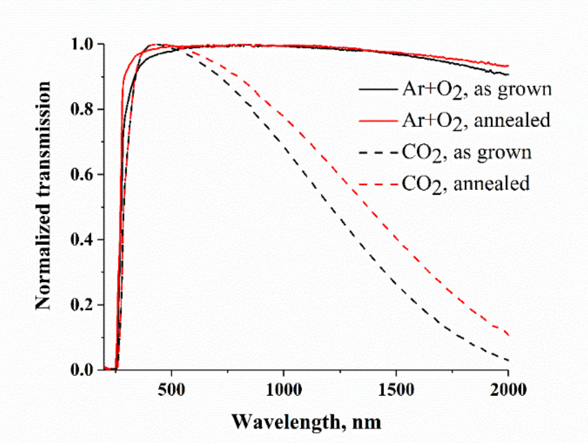

Fig. 2. Normalized transmission spectra of samples of β-Ga_2O_3.
Solid line – samples grown in Ar+O_2 atmosphere, dashed line - samples grown in CO_2 atmosphere

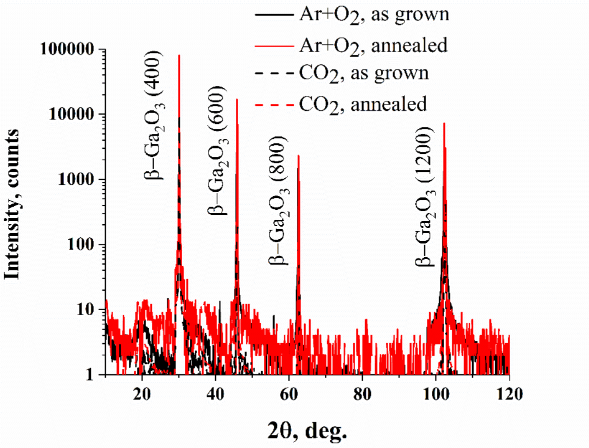

Fig. 3. XRD 2θ-spectra of annealed and non-annealed samples of β-Ga_2O_3.
Solid line – samples grown in Ar+O_2 atmosphere, dashed line - samples grown in CO_2 atmosphere

XRD spectra (Fig. 3) showed the presence of peaks corresponding to the (100) plane of the β-Ga_2O_3 and showed no phase changes between samples. Figures 4 and 5 present normalized rocking curves of samples for peak (400). For sample grown in the Ar+O_2 atmosphere we can see significant reduction in the full width at half maximum (FWHM) of the rocking curve (RC) from $FWHM_{na}$ = 208 arcsec for the non-annealed sample to $FWHM_a$ = 84 arcsec for the annealed one.

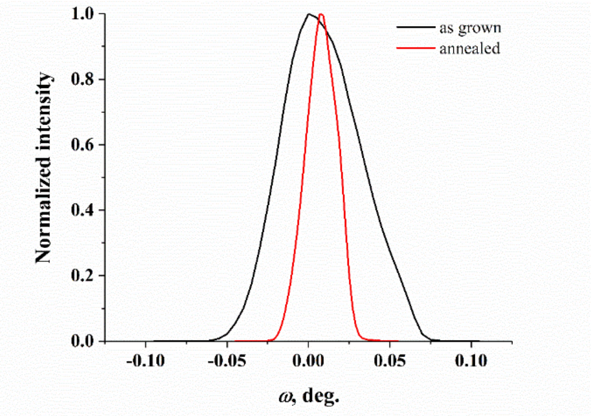

Fig. 4. Rocking curve ω for the peak (400) of annealed and non-annealed samples of β-Ga_2O_3 grown in Ar+O_2 atmosphere. $FWHM_{na}$=208 arcsec, $FWHM_a$= 84 arcsec

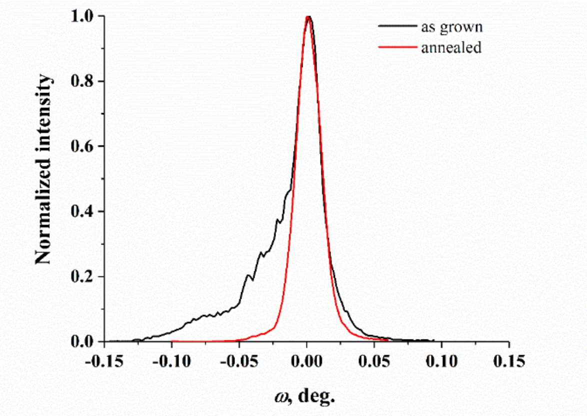

Fig. 5. Rocking curve ω for the peak (400) of annealed and non-annealed samples of β-Ga_2O_3 grown in CO_2. $FWHM_{na}$=82 arcsec, $FWHM_a$= 80 arcsec

Together with the visible change in the morphology of the sample surface after annealing, we can say about the movement of defects on to the surface and an increase in the bulk crystalline quality.

For the sample grown in CO_2 before annealing, a wide tail is observed on the RC, which indicates the presence of defect blocks in the crystal. The RC of the non-annealed sample can be decomposed by gaussians to the three peaks (see Fig. 6), similar to how it was done in [36], which means the presence of multiple disoriented blocks. After annealing, this tail disappears, which shows a decrease in the number of defects i.e., an improvement in crystal quality. The FWHM of RC after annealing correspond to the FWHM of strongest peak at the RC of the non-annealed sample.

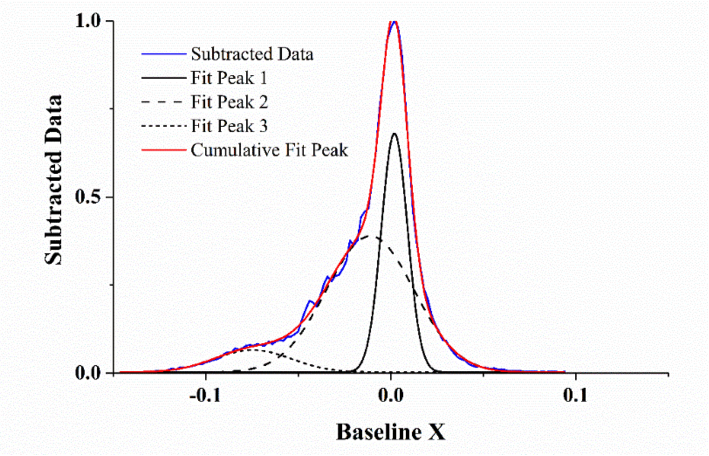

Fig. 6. Decomposition of rocking curve ω for the peak (400) of non-annealed sample β-Ga_2O_3 grown in CO_2 atmosphere by gaussians

Conclusions

The work showed that annealing of β-Ga_2O_3 bulk crystals in air at 1400 °C for 5 hours leads to an increase in transmission in the infrared region of the electromagnetic spectrum and a decrease in the width of the rocking curve, which indicates a decrease in the number of defects in crystal. As has been shown in [35] oxygen vacancies can serve as absorption centers in a gallium oxide. Thus, the increase in transmittance in the IR region can be explained by a decrease in the concentration of oxygen vacancies during annealing in an oxygen-containing atmosphere (in air). RC shows that after annealing FWHM is almost same for samples grown in CO_2 and Ar+O_2 (95:5 vol. %) atmosphere, which means that after annealing, the quality of the sample obtained in the atmosphere of CO_2, which was initially lower, became comparable to the quality of the sample obtained in the atmosphere of Ar+O_2. In general, it can be concluded that annealing leads to a significant improvement in the quality of the samples regardless of the growth atmosphere, although the sample grown in CO_2 still shows higher absorbance in IR range of electromagnetic spectrum.

References

1. Tsao JY, Chowdhury S, Hollis MA, Jena D, Johnson NM, Jones KA, Kaplar RJ, Rajan S, Van de Walle CG, Bellotti E, Chua CL, Collazo R, Coltrin ME, Cooper JA, Evans KR, Graham S, Grotjohn TA, Heller ER, Higashiwaki M, Islam MS, Juodawlkis PW, Khan MA, Koehler AD, Leach JH, Mishra UK, Nemanich RJ, Pilawa-Podgurski RCN, Shealy JB, Sitar Z, Tadjer MJ, Witulski AF, Wraback M, Simmons JA. Ultrawide-Bandgap Semiconductors: Research Opportunities and Challenges. *Advanced Electronic Materials*. 2018;4(1): 160.
2. Wong MH, Bierwagen O, Kaplar RJ, Umezawa H. Ultrawide-bandgap semiconductors: An overview. *Journal of Materials Research*. 2021;36(23): 4601–4615.
3. Woo K, Bian Z, Noshin M, Martinez RP, Malakoutian M, Shankar B, Chowdhury S. From wide to ultrawide-bandgap semiconductors for high power and high frequency electronic devices. *J. Phys. Mater*. 2024;7(2): 022003.
4. Feng T, Zhou H, Cheng Z, Larkin LS, Neupane MR. A Critical Review of Thermal Boundary Conductance across Wide and Ultrawide Bandgap Semiconductor Interfaces. *ACS Appl Mater Interfaces*. 2023;15(25): 29655–29673.
5. Patrick L, Hamilton DR, Choyke WJ. Growth, Luminescence, Selection Rules, and Lattice Sums of SiC with Wurtzite Structure. *Phys Rev*. 1966;143(2): 526–536.
6. Levinshtein ME, Rumyantsev SL, Shur MS. *Properties of Advanced Semiconductor Materials: GaN, AIN, InN, BN, SiC, SiGe*. John Wiley & Sons; 2001.
7. Orita M, Ohta H, Hirano M, Hosono H. Deep-ultraviolet transparent conductive β-Ga2O3 thin films. *Appl. Phys. Lett.* 2000;77(25): 4166–4168.
8. Panov DI, Spiridonov VA, Zakgeim DA, Kremleva AV, Bauman DA, Romanov AE, Bougrov VE. Growth Technology and Optical Properties of Bulk Crystalline Gallium Oxide. *Rev. Adv. Mater. Tech*. 2020;2(3): 51–55.
9. Zhang J, Shi J, Qi DC, Chen L, Zhang KHL. Recent progress on the electronic structure, defect, and doping properties of Ga2O3. *APL Materials*. 2020;8(2): 020906.
10. Green AJ, Chabak KD, Heller ER, Fitch RC, Baldini M, Fiedler A, Irmscher K, Wagner G, Galazka Z, Tetlak SE, Crespo A, Leedy K, Jessen GH. 3.8-MV/cm Breakdown Strength of MOVPE-Grown Sn-Doped β-Ga2O3 MOSFETs. *IEEE Electron Device Letters*. 2016;37(7): 902–905.
11. Bauman DA, Borodkin AI, Petrenko AA, Panov DI, Kremleva AV, Spiridonov VA, Zakgeim DA, Silnikov MV, Odnoblyudov MA, Romanov AE, Bougrov VE. On improving the radiation resistance of gallium oxide for space applications. *Acta Astronautica*. 2021;180: 125–129.
12. Singh R, Lenka TR, Panda DK, Velpula RT, Jain B, Bui HQT, Nguyen HPT. The dawn of Ga2O3 HEMTs for high power electronics - A review. *Materials Science in Semiconductor Processing*. 2020;119: 105216.
13. Shimamura K, Villora E. Czochralski-Based growth and characteristics of selected novel single crystals for optical applications. *Acta Physica Polonica A*. 2013;124(2): 265–273.
14. Blevins JD, Thomson D, Stevens K, Foundos G. Growth of single crystal beta-gallium oxide (β-Ga2O3) semiconductor material. In: *Proceedings of the CSMANTECH*. Indian wells, CA, USA; 2017. p.22–25.
15. Vasil'tsiv VI, Zakarko YaM. Effects of electron capture by impurity centers on the luminescent parameters of β-Ga2O3:Cr crystals. *J. Appl. Spectrosc*. 1983;39(3): 1037–1041.
16. Galazka Z, Uecker R, Irmscher K, Albrecht M, Klimm D, Pietsch M, Brützam M, Bertram R, Ganschow S, Fornari R. Czochralski growth and characterization of β-Ga2O3 single crystals. *Crystal Research and Technology*. 2010;45(12): 1229–1236.
17. Tomm Y, Reiche P, Klimm D, Fukuda T. Czochralski grown Ga2O3 crystals. *Journal of Crystal Growth*. 2000;220(4): 510–514.
18. Panov DI, Spiridonov VA, Zakgeim DA, Kremleva AV, Bauman DA, Romanov AE, Bougrov VE. Growth technology and characterization of bulk crystalline gallium oxide. *J. Phys: Conf. Ser*. 2020;1695(1): 012024.
19. McCloy JS, Jesenovec J, Dutton BL, Pansegrau C, Remple C, Weber MH, Swain S, McCluskey M, Scarpulla M. Growth and defect characterization of doped and undoped β-Ga2O3 crystals. In: *Oxide-based Materials and Devices XIII*. San Francisco, California, United States: SPIE; 2022. p.21–39.
20. Nakai K, Nagai T, Noami K, Futagi T. Characterization of defects in β-Ga2O3 single crystals. *Jpn. J. Appl. Phys*. 2015;54(5): 051103.
21. Kuramata A, Koshi K, Watanabe S, Yamaoka Y, Masui T, Yamakoshi S. High-quality β-Ga2O3 single crystals grown by edge-defined film-fed growth. *Jpn. J. Appl. Phys*. 2016;55(12): 1202A2.
22. Tang H, He N, Zhang H, Liu B, Zhu Z, Xu M, Chen L, Liu J, Ouyang X, Xu J. Inhibition of volatilization and polycrystalline cracking, and the optical properties of β-Ga2O3 grown by the EFG method. *CrystEngComm*. 2020;22(5): 924–931.
23. Zhang S, Lian X, Ma Y, Liu W, Zhang Y, Xu Y, Cheng H. Growth and characterization of 2-inch high quality β-Ga2O3 single crystals grown by EFG method. *J. Semicond*. 2018;39(8): 083003.
24. Mu W, Jia Z, Yin Y, Hu Q, Li Y, Wu B, Zhang J, Tao X. High quality crystal growth and anisotropic physical characterization of β-Ga2O3 single crystals grown by EFG method. *Journal of Alloys and Compounds*. 2017;714: 453–458.

25. Bauman DA, Panov DIu., Spiridonov VA, Kremleva AV, Asach AV, Tambulatova EV, Sakharov AV, Romanov AE. High quality β-Ga2O3 bulk crystals, grown by edge-defined film-fed growth method: Growth features, structural, and thermal properties. *Journal of Vacuum Science & Technology A*. 2023;41(5): 053203.

26. Li P, Han X, Chen D, Sai Q, Qi H. Effect of air annealing on the structural, electrical, and optical properties of V-doped β-Ga2O3single crystals. *Journal of Alloys and Compounds*. 2022;908: 164590.

27. Irmscher K, Galazka Z, Pietsch M, Uecker R, Fornari R. Electrical properties of β-Ga2O3 single crystals grown by the Czochralski method. *Journal of Applied Physics*. 2011;110(6): 063720.

28. Tadjer MJ, Freitas JA, Culbertson JC, Weber MH, Glaser ER, Mock AL, Mahadik NA, Schmieder K, Jackson E, Gallagher JC, Feigelson BN, Kuramata A. Structural and electronic properties of Si- and Sn-doped (−201) β-Ga2O3 annealed in nitrogen and oxygen atmospheres. *J. Phys. D: Appl. Phys*. 2020;53(50): 504002.

29. Okada A, Nakatani M, Chen L, Ferreyra RA, Kadono K. Effect of annealing conditions on the optical properties and surface morphologies of $(\bar{2}01)$-oriented β-Ga2O3 crystals. *Applied Surface Science*. 2022;574: 151651.

30. Bauman DA, Panov DIu, Zakgeim DA, Spiridonov VA, Kremleva AV, Petrenko AA, Brunkov PN, Prasolov ND, Nashchekin AV, Smirnov AM, Odnoblyudov MA, Bougrov VE, Romanov AE. High-Quality Bulk β-Ga2O3 and β-(Al x Ga1−x)2O3 Crystals: Growth and Properties. *Physica Status Solidi (a).* 2021;218(20): 2100335.

31. Galazka Z, Irmscher K, Uecker R, Bertram R, Pietsch M, Kwasniewski A, Naumann M, Schulz T, Schewski R, Klimm D, Bickermann M. On the bulk β-Ga2O3 single crystals grown by the Czochralski method. *Journal of Crystal Growth*. 2014;404: 184–191.

32. Zhang N, Liu H, Sai Q, Shao C, Xia C, Wan L, Feng ZC, Mohamed HF. Structural and electronic characteristics of Fe-doped β-Ga2O3 single crystals and the annealing effects. *J. Mater. Sci*. 2021;56(23): 13178–13189.

33. Jesenovec J, Weber MH, Pansegrau C, McCluskey MD, Lynn KG, McCloy JS. Gallium vacancy formation in oxygen annealed β-Ga2O3. *Journal of Applied Physics*. 2021;129(24): 245701.

34. Schneider SJ, Waring JL. Phase Equilibrium Relations in the Sc2O3-Ga2O3 System. *J. Res. Natl. Bur. Stand. A Phys. Chem*. 1963;67A(1): 19–25.

35. Dong L, Jia R, Xin B, Peng B, Zhang Y. Effects of oxygen vacancies on the structural and optical properties of β-Ga2O3. *Sci Rep*. 2017;7(1): 40160.

36. Bauman DA, Panov DYu, Spiridonov VA, Ivanov AYu, Sakharov AV, Rodin SN, Prasolov ND, Romanov AE. Ob uspeshnom opyte gomoepitaksii sloyev β-Ga2O3 na sobstvennykh podlozhkakh. *Pisma v ZhTF*. 2024;50(7): 43–46. (In Russian)

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