

Investigation of van der Waals crystals of GaSe and GaS_xSe_{1-x} by photoreflectance method

© S.A. Khakhulin¹, K.A. Kokh^{2,3}, O.S. Komkov¹

¹ St. Petersburg Electrotechnical University „LETI“,
197376 St. Petersburg, Russia

² Sobolev Institute of Geology and Mineralogy, Siberian Branch Russian Academy of Sciences,
630090 Novosibirsk, Russia

³ Kemerovo State University,
650000 Kemerovo, Russia

E-mail: khsnm@ya.ru, okomkov@yahoo.com

Received November 30, 2021

Revised December 14, 2021

Accepted December 14, 2021

Photoreflectance spectra of layered undoped GaSe and GaS_xSe_{1-x} crystals present Franz–Keldysh oscillations indicating the near-surface built-in electric field, that can participate in the separation of photoinduced charge carriers in ultrahigh-sensitive photodetectors based on these materials. The measured value of the field strength in GaS_xSe_{1-x} turned out to be almost 1.5 times less than in GaSe, that may indicate a smaller number of free charge carriers in the solid solution. The broadening parameter of GaS_xSe_{1-x} spectral lines is also significantly lower than in the case of GaSe. This is due to the fact that isovalent atoms, being added into the GaSe, fill Ga vacancies, reducing the number of defects and the concentration of intrinsic charge carriers. The high-field modulation mode observed in the photoreflectance spectrum of GaS_xSe_{1-x} doped with an Al donor impurity indicates a relatively small thickness of the depletion region due to the presence of a large number of free electrons.

Keywords: photoreflectance, Franz–Keldysh oscillations, GaSe, gallium monoselenide, van der Waals crystals, layered crystals.

DOI: 10.21883/SC.2022.04.53236.9778

1. Introduction

The study of graphene-like semiconductor crystals is one of the topical directions in the field of modern electronic technology materials [1–5]. Such semiconductors include gallium monoselenide (GaSe), consisting of tetralayers, inside which atomic layers in the order Se-Ga-Ga-Se are covalently bonded, while individual tetralayers are interconnected by weak van der Waals forces. Such a crystal structure allows to layer the material in plane (0001) and obtain single two-dimensional tetralayers [6]. On the basis of such two-dimensional GaSe, a highly efficient detector of optical radiation of visible and ultraviolet spectrum regions with a maximum sensitivity of 2.8 A/W (with a wavelength of 254 nm) and an extremely high claimed quantum efficiency [7] was created. Besides, on the basis of several GaSe tetralayers, prototypes of photodetectors with a sensitivity of ~ 1000 A/W at a wavelength of 400 nm [8] were created. In addition, 2D GaSe crystals can be used to create promising high-frequency *p*-channel field-effect transistors [9] capable of making a complementary pair to *n*-channel graphene-based transistors.

Due to its layered structure, GaSe has a strong optical properties anisotropy: the values of the refractive and absorption indices along the crystal optical axis and in the plane perpendicular to it are significantly different [10], that caused the wide use of GaSe in nonlinear optics devices [11].

The growth of layered chalcogenides crystals of IIIA group post-transition metals, which include GaSe, is mainly carried out using chemical transport reactions method [12] or Bridgman–Stockbarger method [13]. However, it should be noted that GaSe crystals are still of limited use, since in their pure form they contain many defects: point defects in the form of Ga vacancies, as well as microdefects in the form of Ga inclusions, dislocations, and disturbances in the atoms packing in a crystal [14]. The dislocation density can reach 10^9 cm⁻² [15]. Due to the high content of defects, GaSe hardness in the directions other than the main crystallographic axis *c* has a Mooss scale value close to zero [16]. As a result, the quality of the bulk material surfaces outside the plane (0001) limits its use in optical devices [17].

To assess the relative defectiveness of the crystal structure of the obtained crystals, it is desirable to use non-destructive diagnostic methods. For this purpose optical photoreflectance spectroscopy [18] can be used. Besides, using this method, it is also possible to determine the near-surface electric-field intensity without contacts. Such a built-in field in gallium monoselenide, if present, can be used to separate photoinduced charge carriers that appear when the material interacts with light. This makes this material promising for use in photodetectors, since it allows not to create *p*–*n* homo- and heterojunctions traditionally used to separate electrons and holes.

2. Examined samples and experimental procedure

A part of the studied GaSe samples was grown by „2D Semiconductors“ using Bridgman method. Another series of samples was grown in the crystal growth laboratory of V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences. In the second case, a modified Bridgman method was used, in which the plane (0001) of the grown crystal is close to or perpendicular to the growth axis [19]. This series, in addition to pure crystals, contained GaSe samples with several mass percent of sulfur added during growth, that resulted in the formation of GaS_xSe_{1-x} solid solutions. Some GaS_xSe_{1-x} samples were doped with aluminum. Due to the addition of isovalent atoms (S, Al) to the GaSe lattice, the number of Ga vacancies and other possible defects significantly reduces, that results in the improvement of crystal structural quality [20,21]. Besides, adding S into the lattice of nonlinear optical GaSe leads to an increase in the efficiency of frequency conversion using this crystal in the mid-IR range up to 15 times [22]. Aluminum is a donor of free electrons, its addition compensates intrinsic GaSe *p*-conductivity, reducing the charge carrier concentration by 5–7 orders [22].

The photoreflectance (PR) method used in this study is a kind of modulation optical spectroscopy [18], which allows to determine without contact the electric-field intensity and the position of the Fermi level in the near-surface region of semiconductor crystals [23,24], the concentration of free charge carriers [25] etc. Photoreflectance spectroscopy can also be used to estimate the degree of interaction between epitaxial layers of graphene-like crystals with a substrate [26] in the course of their growth using molecular beam epitaxy method [27].

The PR signal is formed by modulating the near-surface electric field by interrupted at a given frequency optical radiation source (usually a laser) with photon energy greater than the band gap of the material under study. As a result of such a periodic action, the reflection (*R*) of the probe beam changes: the value measured in this method is the difference between the crystal reflection coefficients in the absence and presence of laser illumination ($R_{\text{off}} - R_{\text{on}}$), scaled as per the normal reflection coefficient of the material under study R_{off} .

Depending on the built-in near-surface field intensity, three modulation modes [28] are distinguished:

- low-field, when the built-in electric field has a relatively small intensity. In the PR spectrum, there is a single oscillation corresponding to the optical transition „valence band–conduction band“;

- intermediate-field, when, in addition to the signal corresponding to the band gap energy, damped oscillations, called Franz–Keldysh oscillations, are observed in the PR spectrum. Their period can be used to determine the value of the electric field intensity in the near-surface semiconductor region;

- high-field, when the near-surface electric field in the course of modulation changes from the maximum value to zero in the region of signal formation, as a result of which the photoreflectance spectrum is broadened and the oscillating structure disappears.

The study [29] demonstrates the results of investigation of post-transition metal chalcogenides, in particular GaSe, using various optical methods, including photoreflectance spectroscopy. Besides, in this study the emphasis is made on determining the band gap value, and the near-surface electric field is not discussed.

In the study presented here, the spectra were measured using a PR setup assembled on the basis of diffraction spectrometer IKS-31. The source of modulating radiation was a highly stable violet laser SSP-DHS-405 with an operating wavelength of $\lambda = 405$ nm. The intensity of the monochromatic light beam reflected from the same sample region, where the modulating laser radiation was directed was recorded using a silicon photodiode, a preamplifier, and a lock-in amplifier SR830.

3. Results and discussion

Fig. 1 shows photoreflectance spectra of GaSe samples #A (Institute of Geology and Mineralogy and #B („2D Semiconductors“). In case of the PR spectrum of GaSe #A, the solid line shows the type of the signal after processing by the method of apodization of high harmonics of the fast Fourier transform result. Dots show initial experimental data.

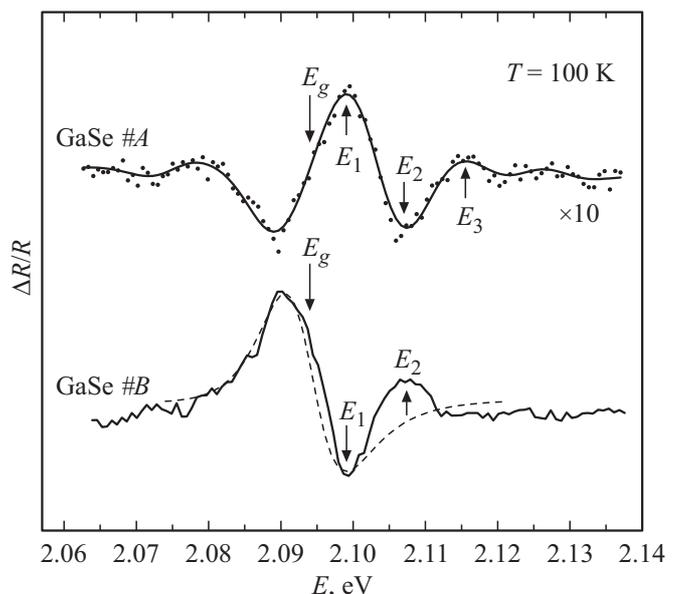


Figure 1. Photoreflectance spectra of undoped GaSe samples. The solid arrows indicate the observed extremes of the Franz–Keldysh oscillations E_j ($j = 1, 2, 3$), as well as E_g from [30]. The dashed line shows the theoretical spectrum constructed according to the low-field model [31].

The PR spectrum of the GaSe sample #A contains Franz–Keldysh oscillations (FKO), the extrema of which are indicated by arrows in the figure and defined as E_1 , E_2 , and E_3 . This is the intermediate-field modulation mode, in which based on the period of the observed oscillations the calculation of the built-in electric field intensity in the near-surface crystal region is possible.

The sample #B spectrum contains two FKO extrema, indicated by arrows. Due to the broadening effects, the remaining extrema turned out to be smoothed out. Assuming the intermediate-field mode, one can also calculate the electric field intensity. This assumption is true from the point of view that the PR signal in the low-field mode would have a different form compared to the one obtained. Fig. 1 shows a comparison of the experimental GaSe #B PR signal with the theoretical spectrum constructed within the framework of the low-field model [31]. The study [31] gives a mathematical description of the spectrum, where the variable parameters that affect its shape are the phase θ , the amplitude C , and the broadening parameter Γ . At the experimental temperature $T = 100$ K, the GaSe band gap is $E_g = 2.094$ eV [30]. By varying the variable parameters, the values $\theta = 5.1$ rad, $\Gamma = 8$ meV, and $C = 10^{-4}$ were obtained, at which the simulated curve almost completely coincides with the experimental signal in the region E_g (see Fig. 1). However, in this case, the theoretical spectrum does not have an extremum, designated for sample #B as E_2 . It should be noted that with the same selected variables, and the phase value $\theta = 0.15$ rad, the theoretical curve has a slightly noticeable extremum in the region of $E_2 = 2.107$ eV, but does not coincide at all with the measured spectrum in shape. The comparison of the theoretical curves with the experiment indicates, that the low-field model is not able to fully describe all the experimental data, and the analysis of the PR spectrum of the #B sample within the mean-field mode is correct.

The FKO period coincides with the period of the function $\cos(2/3((E - E_g)/\hbar\Omega)^{3/2} + \varphi)$, where $\hbar\Omega$ — electro-optical energy, φ — phase factor [32]. To calculate the electric field intensity, the energies of the observed in the PR spectrum FKO extreme values $E_j > E_g$ are determined, where $j = 1, 2, 3$ (see Fig. 1). Then the argument of the previously given cosine is equated to the values $j\pi$ at $E = E_j$, and the expression $(E_j - E_g)^{3/2} = 3/2\hbar\Omega^{3/2}(j\pi - \varphi)$ is obtained. Using the least squares method, line constructed on the points of dependence $(E_j - E_g)^{3/2}$ on number j of FKO extrema, has a slope of m used to determine electro-optic energy $\hbar\Omega = m^{2/3}/2.81$ (meV). The built-in electric field intensity is related to the found energy as $F = 3.24\mu^{1/2}(\hbar\Omega)^{3/2}$ (kV/cm), where μ — reduced effective mass in units of free electron mass m_0 . This method of determining F is described in detail in the study [33]. The reduced effective mass for GaSe is $\mu = 0.178m_0$ [34].

The electric field intensity in the sample #B, determined on two observed FKO extrema, has a value of 11 kV/cm.

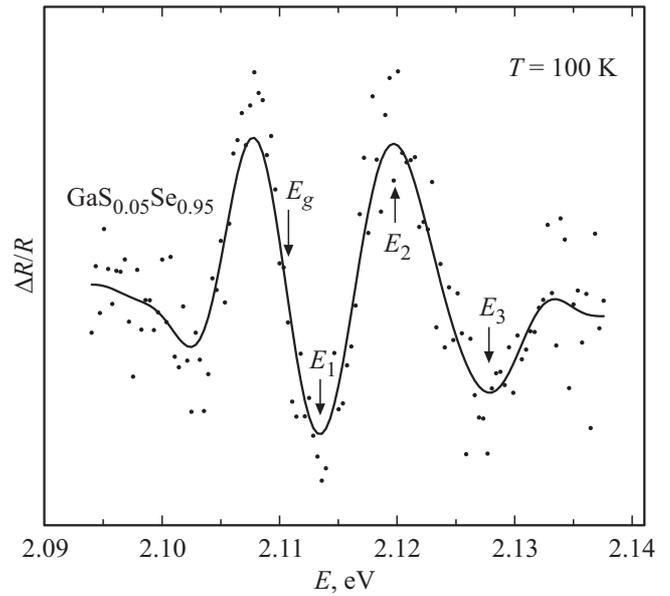


Figure 2. Photorefectance spectrum of $\text{GaS}_{0.05}\text{Se}_{0.95}$ at $T = 100$ K. The intermediate-field modulation mode, in which Franz–Keldysh oscillations are observed, are designated by arrows.

In the #A sample, according to three available extrema, the corresponding intensity was 13 kV/cm. The error of the presented measurements is 0.5 kV/cm.

From the expression describing the spectrum shape in the intermediate-field mode [35], we can express the broadening parameter Γ :

$$\Gamma = \ln \left[\frac{E_2 - E_g}{E_3 - E_g} \cdot \frac{(\Delta R/R)_2}{(\Delta R/R)_3} \right] \times \frac{\hbar\Omega^{3/2}}{(E_3 - E_g)^{1/2} - (E_2 - E_g)^{1/2}}, \quad (1)$$

where $(\Delta R/R)_j$ — the value of the amplitude of the j -th extremum relative to signal zero line, E_j — the value of the energy of j -th extremum. Since, as a result of the broadening effects, the third extremum of the FKO sample #B turned out to be smoothed, the exact value of the Γ parameter cannot be determined. The value of the broadening parameter found according to (1) for the GaSe #A sample was $\Gamma = 7.5$ meV.

The PR spectrum of the $\text{GaS}_{0.05}\text{Se}_{0.95}$ solid solution (1 wt% sulfur) also has the intermediate-field modulation mode (Fig. 2).

The presented PR spectrum was also processed by apodization of high harmonics of fast Fourier transform result. Assuming the temperature dependence of the band gap on the $\text{GaS}_x\text{Se}_{1-x}$ solid solution at small values x of identical dependence for GaSe at the experimental temperature $T = 100$ K the value $E_g(\text{GaS}_{0.05}\text{Se}_{0.95}) = 2.111$ eV [30,36]. The value of the electric field intensity in the near-surface region of the considered crystal $F = 9$ kV/cm, obtained on the base of three FKO extrema, differs from the value in

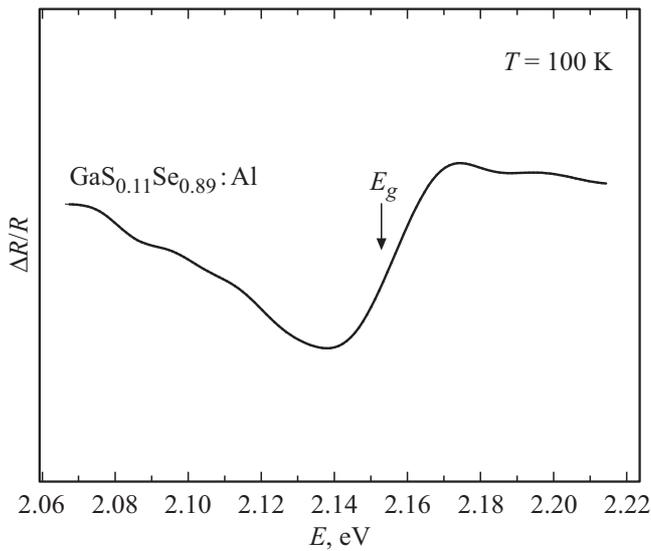


Figure 3. Photoreflectance spectrum of GaS_{0.11}Se_{0.89} doped with Al. High-field modulation mode.

pure GaSe ($F = 13$ kV/cm) by almost 1.5 times. This may be due to the fact that the addition of 1 wt% of sulfur in GaSe significantly reduces the number of free charge carriers (up to 4 orders of magnitude) [37], resulting in an increase in the depletion region and a decrease in the electric field intensity. The broadening parameter Γ for this solid solution, according to (1), was 1 meV, which is several times smaller, than that for GaSe. The result obtained may indicate a much smaller number of defects in the material crystal structure with the addition of a small number of S atoms filling multiple Ga vacancies in GaSe.

Doping of GaS_xSe_{1-x} solid solutions with aluminum leads to a significant increase in the electric field intensity. The PR spectrum of the GaS_{0.11}Se_{0.89}:Al (2.5 wt% of S) sample doped with Al in an amount of 0.02 at% contains strongly broadened along the energy axis single oscillation (Fig. 3).

The presented spectrum corresponds to the high-field modulation mode, in which the averaging of the PR signal over the region of its formation, which occurs in the crystal, leads to a significant broadening of the observed spectrum and the disappearance of the oscillating structure. This indicates the presence of a large amount of dopant and,

The values of the electric field intensity in the near-surface region F , as well as the values of the broadening parameter Γ for the studied samples

Sample	F , kV/cm	Γ , meV
GaSe #A	13	7.5
GaSe #B	11	—
GaS _x Se _{1-x} ($x = 0.05$)	9	1
GaS _x Se _{1-x} :Al ($x = 0.11$)	—	—

as a consequence, a small width of the near-surface region of the space charge [38]. The calculation of the electric field intensity F , as well as the broadening parameter Γ , by the described methods is impossible in this case.

All the values of F and Γ of the studied samples found in the course of the experiments are summarized in the table.

According to calculations, the value of the band gap of the GaS_xSe_{1-x} solid solution in the case of a sample with $x = 0.11$ $E_g(\text{GaS}_{0.11}\text{Se}_{0.89}) = 2.153$ eV [30,36] (indicated by an arrow in Fig. 3), that corresponds to the experimental data.

4. Conclusion

In the course of the study, the photoreflectance spectra of undoped GaSe and GaS_xSe_{1-x} crystals, as well as GaS_xSe_{1-x} samples doped with Al were measured. The PR spectra of GaSe and GaS_xSe_{1-x} have an intermediate-field modulation mode, in within the electric field intensity in the near-surface region of the crystals was found with the help of Franz–Keldysh oscillations. The field intensity in the case of an undoped GaS_xSe_{1-x} $F = 9$ kV/cm sample turned out to be almost 1.5 times less compared to GaSe ($F = 13$ kV/cm). This may be due to the presence of a smaller number of free charge carriers in the solid solution due to the compensation of the intrinsic p - conductivity of GaSe by sulfur atoms. Doping of the GaS_xSe_{1-x} crystal with aluminum leads to a change in the PR modulation mode from intermediate-field to high-field one, as a result the measured spectrum has a broadened form, and the calculation of the field intensity F and the broadening parameter of spectral lines Γ is impossible. The value of Γ in the case of undoped GaS_xSe_{1-x} samples turned out to be significantly lower, compared to GaSe samples (7.5 and 1 meV, respectively). This fact indicates an improvement in the structural properties of gallium monoselenide, when sulfur atoms are added to its crystal lattice. Thus, modulation photoreflectance spectroscopy has demonstrated the possibility of determining the relative defectiveness of van der Waals crystals.

Funding

The works relating to crystal growth were performed under the state assignment of Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences.

Acknowledgments

The authors would like to thank A.O. Mikhin, who helped to measure photoreflectance spectra.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] Q. Tang, A.A. Zhou. *Progr. Mater. Sci.*, **58** (8), 1244 (2013).
- [2] Q. He, Y. Liu, C. Tan, W. Zhai, G.H. Nam, H. Zhang. *ACS Nano*, **13** (11), 12294 (2019).
- [3] Y. Wang, Z. Nie, F. Wang. *Light Sci. Appl.*, **9**, 192 (2020).
- [4] A.J. Watson, W. Lu, M. Guimaraes, M. Söhr. *2D Mater.*, **8** (3), 032001 (2021).
- [5] M. Nayeri, M. Moradinasab, M. Fathipour. *Sci. Technol.*, **33** (2), 025002 (2018).
- [6] Yu.M. Andreev, K.A. Kokh, G.V. Lanskii, A.N. Morozov. *J. Cryst. Growth*, **318** (1), 1164 (2011).
- [7] P.A. Hu, Z. Wen, L. Wang, P. Tan, K. Xia. *ACS Nano*, **6** (7), 5988 (2012).
- [8] Y. Cao, K. Cai, P. Hu, L. Zhao, T. Yan, W. Luo, X. Zhang, X. Wu, K. Wang, H. Zheng. *Sci. Rep.*, **5**, 8130 (2015).
- [9] D.J. Late, B. Liu, J. Luo, A. Yan, H.R. Matte, M. Grayson, C.N.R. Rao, V.P. Dravid. *Adv. Mater.*, **24** (26), 3549 (2012).
- [10] F. Meyer, E.E. De Kluizenaar, D. Den Engelsens. *JOSA*, **63** (5), 529 (1973).
- [11] L. Karvonen, A. Säynätjoki, S. Mehravar, R.D. Rodriguez, S. Hartmann, D.R.T. Zahn, S. Honkanen, R.A. Norwood, N. Peyghambarian, K. Kieu, H. Lipsanen, J. Riikonen. *Sci. Rep.*, **5**, 10334 (2015).
- [12] T. Afaneh, A. Fryer, Y. Xin, R.H. Hyde, N. Kapuruge, H.R. Gutierrez. *ACS Appl. Nano Mater.*, **3** (8), 7879 (2020).
- [13] H. Cai, Y. Gu, Y.C. Lin, Y. Yu, D.B. Geohegan, K. Xiao. *Appl. Phys. Rev.*, **6** (4), 041312 (2019).
- [14] V.I. Shtanov, A.A. Komov, M.E. Tamm, D.V. Atrashenko, V.P. Zlomanov. *Dokl. Chem.*, **361** (1–3), 140 (1998).
- [15] A. Rizzo, C. de Blasi, M. Catalano, P. Cavaliere. *Phys. Status Solidi A*, **105** (1), 101 (1988).
- [16] V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikogosyan. *Handbook for Nonlinear Optical Crystals*, 3rd edn (Berlin, Springer, 1999).
- [17] J.F. Molloy, M. Naftaly, Yu. Andreev, K. Kokh, G. Lanskii, V. Svetlichnyi. *Optical Mater. Express*, **4** (11), 2451 (2014).
- [18] O.S. Komkov. *Phys. Sol. St.*, **63** (8), 1135 (2021).
- [19] K.A. Kokh, J.F. Molloy, M. Naftaly, Yu.M. Andreev, V.A. Svetlichnyi, G.V. Lanskii, I.N. Lapin, T.I. Izaak, A.E. Kokh. *Mater. Chem. Phys.*, **154**, 152 (2015).
- [20] Z. Feng, J. Guo, Z. Kang, Y. Jiang, J. Gao, J. Xie, L. Zhang, V. Atuchin, Y. Andreev, G. Lanskii, A. Shaiduko. *Appl. Phys. B*, **108** (3), 545 (2012).
- [21] J. Guo, D.J. Li, J.J. Xie, L.M. Zhang, Z.S. Feng, Yu.M. Andreev, K.A. Kokh, G.V. Lanskii, A.I. Potekaev, A.V. Shaiduko, V.A. Svetlichnyi. *Laser Phys. Lett.*, **11** (5), 055401 (2014).
- [22] J. Guo, J.-J. Xie, D.-J. Li, G.-L. Yang, F. Chen, C.-R. Wang, L.-M. Zhang, Yu.M. Andreev, K.A. Kokh, G.V. Lanskii, V.A. Svetlichnyi. *Light Sci. Appl.*, **4** (12), 362 (2015).
- [23] J.S. Hwang, C.C. Chang, M.F. Chen, C.C. Chen, K.I. Lin, F.C. Tang, M. Hong, J. Kwo. *J. Appl. Phys.*, **94** (1), 348 (2003).
- [24] X. Yin, H.M. Chen, F.H. Pollak, Y. Chan, P.A. Montano, P.D. Kirchner, G.D. Pettit, J.M. Woodall. *J. Vac. Sci. Technol. A*, **10** (1), 131 (1992).
- [25] O.S. Komkov, A.N. Pikhtin, Yu.V. Zhilyaev, L.M. Fyodorov. *Tech. Phys. Lett.*, **34** (1), 37 (2008).
- [26] O.S. Komkov, S.A. Khakhulin, D.D. Firsov, P.S. Avdienko, I.V. Sedova, S.V. Sorokin. *Semicond.*, **54** (10), 1198 (2020).
- [27] S.V. Sorokin, P.S. Avdienko, I.V. Sedova, D.A. Kirilenko, V.Y. Davydov, O.S. Komkov, D.D. Firsov, S.V. Ivanov. *Materials*, **13** (16), 3447 (2020).
- [28] D.E. Aspnes. *Surf. Sci.*, **37**, 418 (1973).
- [29] S.J. Zelewski, R. Kudrawiec. *Sci. Rep.*, **7** (1), 15365 (2017).
- [30] M. Kepinska, Z. Kovalyuk, R. Murri, M. Nowak. *3rd Int. Conf. Novel Applications of Wide Bandgap Layers' Abstract Book* (Cat. No. 01EX500) (Zakopane, Poland, 2001) p. 146.
- [31] T.J.C. Hosea. *Phys. Status Solidi B*, **189**, 531 (1995).
- [32] O.S. Komkov, G.F. Glinskii, A.N. Pikhtin, Y.K. Ramgolam. *Phys. Status Solidi A*, **206** (5), 842 (2009).
- [33] P.J. Hughes, B.L. Weiss, T.J.C. Hosea. *J. Appl. Phys.*, **77** (12), 6472 (1995).
- [34] G. Ottaviani, C. Canali, F. Nava, Ph. Schmid, E. Mooser, R. Minder, I. Zschokke. *Sol. St. Commun.*, **14** (10), 933 (1974).
- [35] D.E. Aspnes, A.A. Studna. *Phys. Rev. B*, **7** (10), 4605 (1973).
- [36] O.V. Voevodina, A.N. Morozov, S.Y. Sarkisov, S.A. Bereznyaya, S.V. Korotchenko, D.E. Dikov. *Proc. 9th Russian-Korean Int. Symp. on Science and Technology* (Novosibirsk, Russia, 2005) p. 551.
- [37] V.G. Voevodin, S.A. Bereznyaya, Z.V. Korotchenko, A.N. Morozov, S.Y. Sarkisov, N.C. Fernelius, J.T. Goldstein. *MRS Online Proceedings Library*, **829**, 443 (2004).
- [38] A.N. Pikhtin, M.T. Todorov. *Semicond.*, **27** (7), 628 (1993).